Functionalized Organic Molecules for Monitoring of Toxic Gases and VOCs at Room Temperature

Ph.D. Thesis

By MEENU SHARMA



DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JULY 2024

Functionalized Organic Molecules for Monitoring of Toxic Gases and VOCs at Room Temperature

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY

> by MEENU SHARMA



DEPARTMENT OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JULY 2024



INDIAN INSTITUTE OF TECHNOLOGY INDORE

I hereby certify that the work which is being presented in the thesis entitled Functionalized Organic Molecules for Monitoring of Toxic Gases and VOCs at Room Temperature in the partial fulfillment of the requirements for the award of the degree of DOCTOR OF PHILOSOPHY and submitted in the DEPARTMENT OF CHEMISTRY, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from June 2019 to July 2024 under the supervision of Prof. APURBA K. DAS, Professor, Department of Chemistry, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

11-12-2024

Signature of the student with date (MEENU SHARMA)

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

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Signature of Thesis Supervisor with date (Prof. APURBA K. DAS)



ACKNOWLEDGMENTS

Throughout the entirety of my Ph.D. journey, I extend my appreciation to numerous individuals for their significant contributions, including my mentors, colleagues, scholarship providers, friends, and family.

First and foremost, I would like to express my great appreciation to Professor Apurba Kumar Das, my doctoral research supervisor for his mentorship and constant encouragement during my Ph.D. journey. I am eternally grateful for the experience of working in the Prof. Das group. I'm inspired by his work ethic and proactive approach to tasks, which significantly contributed to my academic experience. Over the past five years, I have acquired extensive knowledge in organic-inorganic nanohybrid and polymeric chemistry, with Prof. Das catalyzing my passion for science and research. I'm grateful for his continuous support, especially during challenging moments, such as shaping the figures for the first paper. His guidance on enhancing the visual appeal of figures to improve manuscript quality has been invaluable. The lab group's shared meals, dinners, and discussions at Indore have added a delightful dimension to my academic journey. Prof. Das, your mentorship has left an indelible mark on my academic and professional journey, and I extend my heartfelt appreciation for the enriching experience.

I would like to extend my gratitude to our collaborators Professor Shaibal Mukherjee and Professor Sharath Sriram. Your assistance was invaluable in helping us to understand the basic electrical engineering principles and try to incorporate chemistries into the sensing devices. The work experience we shared has taught me that it takes interdisciplinary teamwork when trying to produce a final working product. Your valuable advice and comments have always improved the quality of my work.

I want to offer special thanks to PSPC committee members Professor Shaibal Mukherjee, Professor Tushar Kanti Mukherjee and Professor Debasis Nayak for their valuable and constructive suggestions that were very helpful for me in improving the quality of my work during the

i

course of my degree. I am grateful to the faculty members in the Department of Chemistry, Professor Tushar Kanti Mukherjee (Head, Department of Chemistry), Prof. Rajneesh Misra, Prof. Suman Mukhopadhyay, Prof. Sampak Samanta, Prof. Biswarup Pathak, Prof. Sanjay K. Singh, Dr. Tridib K. Sarma, Prof. Anjan Chakraborty, Prof. Shaikh M. Mobin, Dr. Satya S. Bulusu, Prof. Chelvam Venkatesh, Dr. Amrendra K Singh, Dr. Debayan Sarkar, Dr. Abhinav Raghuvanshi, Dr. Dipak K Roy, Dr. Selvakumar Sermadurai, Dr. Umesh A. Kshirsagar and Dr. Pravarthana Dhanapal for their guidance and help during various activities.

I would like to extend my heartfelt appreciation to Prof. Suhas S. Joshi, Director of IIT Indore, for his ongoing encouragement, assistance, and support.

I express my immense gratitude to every member of the supramolecular organic chemistry group, who has supported me throughout my journey. My sincere thanks to both past and current group members Dr. Sayan Maiti, Dr. Pramod Kumar Gavel, Dr. Rohit Jadhav, Dr. Ankan, Dr. Tapas Ghosh, Dr. Devraj Singh, Dr. Deepak K. K. Kori, Mr. Sourav Bhowmik, Ms. Likhi, Mr. Tanmay Rit, Ms. Lalita Wagh, Ms. Arati Samal, Ms. Anushree Jain, Mr. Deepak K. Pandey, Mr. Mithu Roy, Ms. Nikita Sharma, Mr. Sachin Kumar, Ms. Sweta Agarwal, Ms. Shruti Ghosh, Mr. Sudarshan Maji, Mr. Saryu Bhardwaj, Ms. Ayushi Singh, Mr. Chiranjeeb Kundu and Mr. Supratim Ghosh. You all were a tremendous support and a pleasure to work with as we maintained a professional and friendly work environment. We shared some great laughs and insightful conversations which helped me grow as a researcher. I extend my heartfelt thanks to Dr. Chandrabhan K. Patel, Mr. Sumit Chaudhary, Mr. Mayank Dubey, Mr. Ranjhan Mishra, Mr. Vikas K. Verma, and Mr. Ajit Yadav from the HNRG group at IIT Indore for their consistent support and encouragement during my journey.

ii

I am thankful to Mr. Kinney Pandey, Mr. Ghanshyam Bhavsar, Dr. Ravinder, and Mr. Nitin Upadhyay for their help during the instrumental analysis. Mr. Manish Kushwaha, Mrs. Vinita Kothari, and Mr. Rameshwar Dauhare are also acknowledged for their technical help and support.

I like to acknowledge the Council of Scientific & Industrial Research (CSIR) for providing me with a fellowship, which helped me to buy chemical and living expenses. I also thank the sophisticated Instrument Centre at the Indian Institute of Technology Indore (SIC IIT Indore) for providing me with all the instrumentation facilities required during my Ph.D. study. I would like to thank the Indian Institute of Technology Indore (IIT Indore) for providing me with the Indian Institute of Technology Bombay (IIT Bombay), Indian Institute of Technology Jammu (IIT Jammu), Indian Institute of Technology Gandhinagar (IIT Gandhinagar), and Indian Institute of Science Education and Research Thiruvananthapuram (IISER TVM) for providing me HR TEM, XPS, MALDI, and solid-state NMR facilities during my work.

I would like to thank my parents, Mrs. Neeraj Sharma (mother) and Mr. Dinesh Kumar Sharma (father). You both were my first mentors in my life and provided me with the resources to be successful. I could not have achieved this much without your patience, advice, support, and unconditional love. Also, I thank my brother for his constant encouragement throughout my Ph.D and in my life. Sincere thanks to my beloved husband Mr. Prashant Pathak and in-laws for their constant support. Their encouragement and understanding have been a constant source of strength throughout this journey. I feel so lucky to have such an amazing, caring family who always supports and loves me, thank you.

Meenu Sharma

Dedicated to

My Family

ABSTRACT

The rise of industrialization and population has directly hastened air pollution, due to the emission of toxic gases or volatile organic compounds (VOCs). These hazardous gases or VOCs directly or indirectly pose serious threats to the environment and human health. Consequently, the detection of these harmful gases has gained paramount importance. Therefore, there is a need to develop a gas or VOC sensor that can identify toxic gases or VOC molecules in the surroundings. Thus, the development of high-quality, low-power-consuming, and affordable gas sensors has become a crucial societal demand for the real-time monitoring of toxic and inflammable gases or VOCs. This demand requires advanced functionalized sensing materials, such as conjugated polymers and organic-inorganic hybrids, which offer increased sensitivity and efficiency at room temperature (RT). Conjugated polymers and organic-inorganic hybrid materials have emerged as promising sensing materials due to their unique properties, such as high sensitivity, selectivity, stability, reproducibility, and the ability to operate at room temperature.

In this thesis, I have focused on designing and synthesizing functionalized organic molecules including conjugated polymers and organic-inorganic hybrid materials. These functionalized organic molecules will serve as active functional sensing materials for chemiresistive sensors. These sensing materials have the potential to detect toxic gases or VOCs with high sensitivity and selectivity in various environments.

The primary objectives of my current research are as follows:

- To design and synthesize covalent organic polymers, whose backbones were functionalized with amide or thioamide functional groups for the detection of H₂S at 25 °C.
- ✤ To design and synthesize conjugated polymers with backbones containing benzoselenadiazole and thiazole for the detection of SO₂ at 25 °C.

- To design and synthesize imine-linkage nanoporous covalent organic polymers (nCOPI), subsequently imine bonds were reduced to amine linkage nanoporous covalent organic polymer (nCOPA) and employed for the detection of NH₃ at 25 °C.
- ★ To design and develop the NDICY-ZnO nanohybrid (NDI = naphthalenediimide, C = 6-aminocaproic acid, Y = L-tyrosine) *via* a single-pot method for the detection of ethanol at 27 °C.

1. Investigating the Role of Amide to Thioamide Substitution of a Covalent Organic Polymer for the Selective Chemodetection of H₂S at Room Temperature

The demand for hydrogen sulfide (H₂S) sensors significantly rising due to their importance in diagnosing metabolic diseases and monitoring environmental pollution. Covalent organic polymers (COPs) are gaining interest in gas sensing due to their unique features, including high surface area, porous characteristics, lightweight, and operation at RT. Herein, I have designed and synthesized two covalent organic polymers (COPs), in which the backbone was functionalized with amide (COPO) and thioamide (COPS) bonds and characterized through various techniques. Furthermore, COPO and COPS were employed as sensing materials for the selective detection of H₂S at 25 °C. The COPO sensor exhibited a response 2.6 times higher, reaching 190%, to 100 ppm of H_2S , with a rapid response/recovery time of 20/40 s, in comparison to COPS (response = 73%). The COPO sensor exhibited a linear increment in the response value with an increase in concentration. The COPO sensor also exhibited remarkable selectivity against other toxic gases with limit of detection (LOD) and limit of quantification (LOQ) values of 0.75 ppb and 2.5 ppb, respectively. The sensing mechanism of COPO and COPS was proposed based on the hydrogen bonding between H₂S and NH of amide or thioamide bonds, which inhibits the conduction of proton in the COP. Accordingly, the resistance of COP sensors increased and the response was calculated. The above-discussed results suggest the

diverse applications of COPO in industries and environmental monitoring.

2. Tailoring Thiazole Decorated Polymer with Benzoselenadiazole for Enhanced SO₂ Sensing

Sulfur dioxide (SO_2) poses a threat to both human health and the environment. Nevertheless, the progress in the development of SO₂ sensors operating effectively at RT has been significantly limited due to their insufficient recovery capabilities. Conjugated polymers (CPs) incorporated with benzoselenodiazole/thiazole rings in the backbone of CPs offer significant selectivity towards SO₂ gas in real-time monitoring. Herein, I have designed and developed CP, which was decorated with thiazole rings named BBT. Further, the backbone of BBT CP was functionalized with benzoselenadiazole ring, resulted CP was named BBTBSe and both BBT and BBTBSe were well characterized by different techniques. Furthermore, BBTBSe and BBT were employed for the selective chemodetection of SO₂ at 25 °C. The BBTBSe sensor exhibited a 4.3 fold enhanced response (Rg/Ra) of 199.4 to 100 ppm of SO₂ with a fast response/recovery time of 60/70 s, as compared to BBT (response = 45.7). Thus, the BTBBSe sensor shows excellent selectivity against other interfering gases with a selectivity factor greater than 5.3, complete reversibility, and prolonged stability at 25 °C. Moreover, BBTBSe sensors exhibited a linear increase in the response with concentration. Additionally, the LOD and LOQ values were calculated to be 0.23 and 0.76 ppb, respectively. The plausible mechanism is described on the basis of the interaction of SO₂ molecules on the surface of CPs. The nitrogen atom present in the benzoselenadiazole and thiazole ring increases the basicity of the CP, which offers a large number of active sites for the interaction of SO₂ (acidic gas) molecules. The lone pairs of N would be transferred to S of SO₂, leading to weak dipole-dipole interaction. A significant change in the resistance was observed in the BBTBSe sensor. Impressive outcomes propose a practical method for precise

detection of SO₂ using the BBTBSe sensor, which recommends its industrial and environmental applications.

3. Tailoring NH₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer

In this report, I have synthesized imine-linkage nanoporous covalent organic polymer (nCOPI) and further imine bonds were reduced to an amine-linkage nCOP (nCOPA). nCOPI and nCOPA have been employed for the selective detection of NH₃ at 25 °C. The nCOPA sensor exhibited 18.8 fold enhanced response (R_g/R_a) of 1700% to 500 ppm of NH3 with a fast response/recovery time of 60/70 s, as compared to nCOPI (response = 91%). The nCOPA sensor shows remarkable selectivity against other interfering gases, repeatability, complete reversibility, and long-term durability at 25 °C. Moreover, the response of the nCOPA sensor linearly increases with concentration. Additionally, the LOD and LOQ values were observed to be 0.25 ppb and 0.86 ppb, respectively. The proposed NH₃ sensing mechanism is based on the charge transfer between the NH₃ (which acts as an electron donor) and p-type nCOPA (an electron acceptor), where the holes are the majority carriers. In the NH₃ atmosphere, NH₃ molecules donate their electrons to the holes in nCOPA which reduces the number of holes. This increased the resistance of the nCOPA sensor and the response value was calculated. Additionally, NH₃ molecules may form hydrogen bonds with the NH group of nCOPA, which inhibits the conjugation within the nCOPA backbone. This weakened conjugation causes a decrease in the mobility of charge carriers (holes), resulting in a notable increase in resistance. The impressive outcomes suggest that nCOPA sensors could be employed for precise NH₃ detection in industries and environmental monitoring.

4. Fabricated Chemiresistive Sensor for Detection of Ethanol Using NDICY-ZnO Nanohybrid

Elevated levels of ethanol vapors may serve as a biomarker for fatty liver diseases and can cause significant damage to the nervous system. In this study, I have synthesized an NDICY-ZnO (NDI = naphthalenediimide, C = 6-Aminocaproic acid, Y = L-tyrosine) nanohybrid using a facile single-pot hydrothermal method and characterized it by using various techniques. The NDICY, ZnO, and NDICY-ZnO nanohybrids were used to detect ethanol vapors at 27 °C. The sensing experiment revealed that the NDICY-ZnO nanohybrid exhibited a maximum response of 66.4% towards 500 ppm ethanol, compared to the NDICY and ZnO precursors, which exhibited responses of 17.8% and 19.6%, respectively. It also demonstrates sufficient selectivity towards ethanol vapors over other interfering gases or VOCs. Interestingly, the sensor's performance was improved under humid conditions. Furthermore, the NDICY-ZnO fabricated device exhibited excellent stability and remained steady for 90 days under ambient conditions. The synergistic effect of NDICY-ZnO nanohybrid has resulted in excellent sensitivity and adequate selective behavior towards ethanol, which makes it a promising sensing material for practical applications with outstanding features.

LIST OF PUBLICATION

Publications from PhD Thesis Work

In referred Journals

- Sharma, M., Patel, C., Sriram, S., Mukherjee, S., Das, A. K. (2024), Tailoring NH₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer, ACS Appl. Nano Mater., 7, 12926-12934 (DOI: 10.1021/acsanm.4c1480). (I.F: 5.9)
- Sharma, M., Patel, C., Samal, A., Sriram, S., Mukherjee, S., Das, A. K. (2024), Tailoring Thiazole Decorated Polymer with Benzoselenadiazole for Enhanced SO₂ Sensing, ACS Appl. Polym. Mater., 6, 6937–6945 (DOI: 10.1021/acsapm.4c00427). (I.F: 5)
- Sharma, M., Patel, C., Sriram, S., Mukherjee, S., Das, A. K. (2023), Investigating the Role of Amide to Thioamide Substitution of a Covalent Organic Polymer for the Selective Chemodetection of H₂S at Room Temperature, ACS Appl. Polym. Mater., 5, 10065–10072 (DOI: 10.1021/acsapm.3c01872). (I.F: 5)
- Sharma, M., Patel, C., Maiti, S., Mukherjee S., Das, A. K. (2023), Fabricated Chemiresistive Sensor for Detection of Ethanol Using NDICY-ZnO Nanohybrid, IEEE Sens. J., 23, 15342-15349 (DOI: 10.1109/JSEN.2023.3276771). (I.F: 4.3)

In referred conferences

- <u>Sharma, M.</u>, Das, A. K., Fabricated Chemiresistive Sensor for Detection of Ethanol Using NDICY-ZnO Nanohybrid, Student Research Symposium, August 10-11, 2022 at Department of Electrical Engineering, Indian Institute of Technology, Indore, India, (Oral Presentation).
- Sharma, M., Das, A. K., Tailoring Thiazole Decorated Polymer with Benzoselenadiazole for Enhanced SO₂ Sensing, In-House Chemistry Symposium "CHEM 2023" March 6, 2022 at

Department of Chemistry, Indian Institute of Technology, Indore, India, (Oral Presentation).

- <u>Sharma, M</u>., Das, A. K., Fabricated Chemiresistive Sensor for Detection of Ethanol Using NDICY-ZnO Nanohybrid, Empowering Women in Sensors Technology (EWST'22), December 16, 2022, (Poster Presentation).
- Sharma, M., Das, A. K., Fabricated Chemiresistive Sensor for Detection of Ethanol Using NDICY-ZnO Nanohybrid, Summer School Program Sensors Innovation Towards Emerging Technology workshop, August 5, 2022, (Poster Presentation).
- Sharma, M., Das, A. K., Tailoring NH₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer, CRSI local chapter one-day conference, May 11, 2024 at Department of Chemistry, Indian Institute of Science Education and Research (Poster Presentation).

Other publications during PhD

In referred Journals

 Maiti, S., Mandal, B., Sharma, M., Mukherjee, S., Das, A. K. (2020), Covalent Organic Polymer as an Efficient Chemosensor for Highly Selective H₂S Detection through Proton Conduction. *Chem. Commun.*, 56, 9348-9351 (DOI: 10.1039/D0CC02704A).

TABLE OF CONTENTS

1.	LIST OF FIGURES	xxi
2.	LIST OF SCHEMES	xxxi
3.	LIST OF TABLES	xxxiii
4.	ACRONYMS	XXXV
5.	NOMENCLATURE	xxxvii
Chapter 1: General Introduction		1-56
1.1	Introduction	3
1.1.1	Essential Need for a Gas or Volatile Organic	3
	Compound (VOC) Sensor	
1.1.2	Types of Gas or VOC Sensors	6
1.1.2	1 Resistive Sensor	6
1.1.2	2 Electrochemical Sensor	7
1.1.2	3 Colorimetric Gas Sensor	7
1.1.2	4 Optical Sensors	8
1.1.3	Sensing Parameters	8
1.1.3	1 Response	9
1.1.3	2 Sensitivity	9
1.1.3	.3 Selectivity	9
1.1.3	4 Response time	9
1.1.3	5 Recovery time	10
1.1.3	.6 Dynamic range	10
1.1.3	7 Repeatability	10
1.1.3	.8 Stability	10
1.1.3	9 LOD and LOQ	10
1.1.4	Sensing Mechanism	11
1.1.4	1 Gas Sensing Mechanism for Organic-Inorganic Hybrid	11
1.1.4	2 Gas Sensing Mechanism for Small Organic Molecules	13
	and CP	
1.1.5	Functionalized Organic Molecules in Gas or VOC Sensing	14
1.1.5	1 Gas Sensors Based on Small Organic Molecules	15
1.1.5	2 Gas Sensors Based on Conjugated Polymer	21

1.1.5.3 Gas Sensors Based on Organic-	29
Inorganic Hybrid	
1.2 Summary	35
1.3 Thesis Organization	36
1.4 Reference	37
Chapter 2: Investigating the Role of Amide to	57-84
Thioamide Substitution of a Covalent Organic	
Polymer for the Selective Chemodetection of	
H ₂ S at Room Temperature	
2.1 Introduction	59
2.2 Aims and Objectives	61
2.3 Experimental Section	61
2.3.1 Materials and Methods	61
2.3.2 Synthesis of COPO and COPS	61
2.3.3 Characterization of COPO and COPS	62
2.3.4 H ₂ S Sensor Fabrication	63
2.3.4.1 Device dimensions	63
2.3.4.2 Device fabrication	63
2.3.4.3 Sensing setup and measurements	63
2.4 Results and Discussion	65
2.4.1 H ₂ S Sensing Performance of the COPO and COPS	70
2.4.2 H ₂ S Mechanism	74
2.5 Conclusion	76
2.6 References	76
Chapter 3: Tailoring Thiazole Decorated Polymer	85-122
with Benzoselenadiazole for Enhanced SO ₂ Sensing	
3.1 Introduction	87
3.2 Aims and Objectives	89
3.3 Experimental Section	89
3.3.1 Chemicals and Methods	89
3.3.2 Synthesis of Compounds	90
3.3.2.1 Synthesis of Intermediates and Monomer	90
(4,4'-benzo[c][1,2,5]selenadiazole-4,7-diyl)dibenzonitrile,	
BPBSe)	

3.3.2.1.1 Synthesis of benzo[c][1,2,5]selenadiazole	
(2)	90
3.3.2.1.2 Synthesis of 4,7-dibromobenzo[c][1,2,5]	
selenadiazole (3)	91
3.3.2.1.3 Synthesis of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan	
-2-yl)benzonitrile(5)	93
3.3.2.1.4 Synthesis of 4,4'-benzo[c][1,2,5]selenadiazole	
-4,7-diyl) dibenzonitrile (BPBSe, 6)	94
3.3.2.2 Synthesis of BBTBSe	95
3.3.2.3 Synthesis of BBT	96
3.3.3 Characterization Techniques	96
3.3.4 Device Fabrication and SO ₂ Sensing Evaluation	97
3.4 Results and Discussion	99
3.4.1 SO ₂ Sensing Performance	105
3.4.2 SO ₂ Sensing Mechanism	110
3.5 Conclusion	112
36 References	112
J.0 Kelelelees	
Chapter 4: Tailoring NH ₃ Sensing Responsiveness	123-156
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous	123-156
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer	123-156
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer 4.1 Introduction	123-156 125
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer 4.1 Introduction 4.2 Aims and Objectives	123-156 125 127
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer 4.1 Introduction 4.2 Aims and Objectives 4.3 Experimental Section	123-156 125 127 128
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer 4.1 Introduction 4.2 Aims and Objectives 4.3 Experimental Section 4.3.1 Chemical and Methods	123-156 125 127 128 128
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer 4.1 Introduction 4.2 Aims and Objectives 4.3 Experimental Section 4.3.1 Chemical and Methods 4.3.2 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1"	123-156 125 127 128 128
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer 4.1 Introduction 4.2 Aims and Objectives 4.3 Experimental Section 4.3.1 Chemical and Methods 4.3.2 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1" -terphenyl]-4,4"-dicarbaldehyde (TP3F), Imine	123-156 125 127 128 128
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer 4.1 Introduction 4.2 Aims and Objectives 4.3 Experimental Section 4.3.1 Chemical and Methods 4.3.2 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1" -terphenyl]-4,4"-dicarbaldehyde (TP3F), Imine Linkage Nanoporous Covalent Organic Polymer	123-156 125 127 128 128
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer 4.1 Introduction 4.2 Aims and Objectives 4.3 Experimental Section 4.3.1 Chemical and Methods 4.3.2 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1" -terphenyl]-4,4"-dicarbaldehyde (TP3F), Imine Linkage Nanoporous Covalent Organic Polymer (nCOPI) and Amine Linkage Nanoporous	123-156 125 127 128 128
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer 4.1 Introduction 4.2 Aims and Objectives 4.3 Experimental Section 4.3.1 Chemical and Methods 4.3.2 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1" -terphenyl]-4,4"-dicarbaldehyde (TP3F), Imine Linkage Nanoporous Covalent Organic Polymer (nCOPI) and Amine Linkage Nanoporous Covalent Organic Polymer (nCOPA)	123-156 125 127 128 128 128
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer 4.1 Introduction 4.2 Aims and Objectives 4.3 Experimental Section 4.3.1 Chemical and Methods 4.3.2 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1'' -terphenyl]-4,4''-dicarbaldehyde (TP3F), Imine Linkage Nanoporous Covalent Organic Polymer (nCOPI) and Amine Linkage Nanoporous Covalent Organic Polymer (nCOPA) 4.3.2.1 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1''-terphenyl]	123-156 125 127 128 128 128
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer 4.1 Introduction 4.2 Aims and Objectives 4.3 Experimental Section 4.3.1 Chemical and Methods 4.3.2 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1" -terphenyl]-4,4"-dicarbaldehyde (TP3F), Imine Linkage Nanoporous Covalent Organic Polymer (nCOPI) and Amine Linkage Nanoporous Covalent Organic Polymer (nCOPA) 4.3.2.1 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1"-terphenyl] 4,4"-dicarbaldehyde (TP3F, 3)	123-156 125 127 128 128 128 128
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer 4.1 Introduction 4.2 Aims and Objectives 4.3 Experimental Section 4.3.1 Chemical and Methods 4.3.2 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1" -terphenyl]-4,4"-dicarbaldehyde (TP3F), Imine Linkage Nanoporous Covalent Organic Polymer (nCOPI) and Amine Linkage Nanoporous Covalent Organic Polymer (nCOPA) 4.3.2.1 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1"-terphenyl] 4.3.2.1 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1"-terphenyl] 4.3.2.2 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1"-terphenyl]	123-156 125 127 128 128 128 128
Chapter 4: Tailoring NH ₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer 4.1 Introduction 4.2 Aims and Objectives 4.3 Experimental Section 4.3.1 Chemical and Methods 4.3.2 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1" -terphenyl]-4,4"-dicarbaldehyde (TP3F), Imine Linkage Nanoporous Covalent Organic Polymer (nCOPI) and Amine Linkage Nanoporous Covalent Organic Polymer (nCOPA) 4.3.2.1 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1"-terphenyl] 4,4"-dicarbaldehyde (TP3F, 3) 4.3.2.2 Synthesis of Imine Linkage Nanoporous Covalent Organic Polymer (nCOPI)	123-156 125 127 128 128 128 128 128 129 130

Organic Polymer (nCOPA)	130
4.3.3 Characterization Techniques	
4.3.4 H ₂ S Sensor Fabrication and Characterization	131
4.3.4.1 Device fabrication	131
4.3.4.2 Sensing setup and measurements	
4.4 Results and Discussion	
4.4.1 NH ₃ Sensing Performance	138
4.4.2 Sensing Mechanism	142
4.5 Conclusion	145
4.6 References	
Chapter 5: Fabricated Chemiresistive Sensor	157-196
for Detection of Ethanol Using NDICY-ZnO Nanohybrid	
5.1 Introduction	159
5.2 Aims and Objectives	161
5.3 Experimental Section	161
5.3.1 Materials and Methods	161
5.3.2 Synthesis of the Compounds	162
5.3.2.1 Synthesis of Synthesis of 6-((tert-	
butoxycarbonyl)amino)hexanoic acid (Boc-Cap-OH, 2)	162
5.3.2.2 Synthesis of methyl (6-((tert-butoxycarbonyl)amino)	
hexanoyl)-L-tyrosinate (Boc-Cap-Y-OMe, 5)	164
5.3.2.3 Synthesis of NDICY-OMe	166
5.3.2.4 Synthesis of NDICY	168
5.3.2.5 Synthesis of the NDICY-ZnO Nanohybrid	170
5.3.2.6 Synthesis of the Zinc oxide (ZnO)	171
5.3.2.7 Synthesis of the mechanically grinded NDICY-	171
ZnO Composite	
5.3.3 Characterization Technique	172
5.3.4 Gas Sensor Fabrication and Measurement	172
5.4 Results and Discussion	173
5.4.1 Current-voltage (<i>I–V</i>) analysis	180
5.4.2 Ethanol Sensing Properties of the NDICY-ZnO	181
Nanohybrid	
5.5 Conclusion	188

5.6 References	189
Chapter 6: Conclusions and Future Perspectives	197-203
6.1 Conclusions	199
6.2 Future Perspectives	201

LIST OF FIGURES

Chapter 1: General Introduction

Figure 1.1 Sources of dangerous gases or VOCs and their 4 immediate and prolonged impact on human health.

Figure 1.2 Various kinds of sensors for Gas or VOC detection.
7
Figure 1.3 Various parameters for gases or VOCs sensing,
9
provide diverse methods to detect and analyze environmental toxic analytes.

Figure 1.4 The sensing mechanism of n- and p-type (a) 12 organic-inorganic hybrid and (b) conjugated polymer or small organic compound toward reducing and oxidizing gases or VOCs.

Figure 1.5 (a) Schematic of the fabricated NDI-A device. (b) 16 NDI-A based sensor's response/recovery curve. (c) NDI-A sensor's response to varying NH₃ concentrations. (d) Impact of humidity on NDI-A NH₃ sensing performance. (e) NDI-A sensor's selectivity to NH₃ compared to other gases. (f) Molecular configuration of NDI-CN₄ and NDI-H₄. (g) Device structures of fabricated NDI-CN₄ and NDI-H₄. (h) NH₃ response and recovery times for NDI-CN₄. (i) NDI-CN₄ selectivity against other interfering gases. (j) Dynamic response to NH₃ concentrations from 3 ppm to 50 ppm for NDI-CN₄ sensor and (k) recyclability and long-term durability of NDI-CN₄ sensor toward 50 ppm NH₃.

Figure 1.6 (a) Chemical structure of d-THBPDI. (b) An 18 optimized device utilizing d-THBPDI film for gas-sensing measurements. (c) Response/recovery times of d-THBPDI device towards 100 ppm hydrazine. (d) A device utilizing d-THBPDI film response to hydrazine vapour concentrations ranging from 5 ppm to 200 ppm and (e) repeatability response curve of d-THBPDI to hydrazine vapours.

Figure 1.7 (a) Response of TCPP 1 to 100 ppm NO_2 in dark. 20

(b) Repeatability curve of TCPP 1 towards 100 ppm NO_2 in the visible light. (c) Dynamic response to different concentrations of NO_2 for TCPP **1**. (d) Selectivity graph of TCPP **1** to NO_2 against other gases and (e) the possible sensing mechanism for TCPP **1** to NO_2 .

Figure 1.8 (a) Schematic depiction of the SAPS process for 22 DPP-DTT films. crafting ultrathin nanoporous (b) Responsiveness of DPP-DTT films with different thicknesses to 10 ppm methanol. (c) Comparative bar chart of response and recovery times for different thicknesses of DPP-DTT films. (d) Selectivity curve of bar chart of DPP-DTT films comparing the response/recovery times for 10 ppm MeOH vapour towards different VOCs. (e) Bar chart of DPP-DTT films comparing the response/recovery times for different VOCs. (f) Dynamic response curve to diverse concentrations of MeOH. (g) Repeatability curve of DPP-DTT to different VOCs.

Figure 1.9 (a) Schematic depiction of flexible NO₂ chemoresistive sensor based on IM-x/P-y CP. (b) Dynamic variations in resistance for IM-0.1/P-y sensors with varied PEI dopant weight ratios. (c) Gas sensitivity was observed when exposed to 0.1-1 ppm NO₂ using IM-0.1/P-y sensors with diverse PEI dopant weight ratios. (d) Selectivity of IM-0.1/P-1.0 sensor toward various gas analytes and humidity. (e) Longterm stability toward cyclic exposure to 1 ppm NO₂ gas for IM-0.1/P-1.0 sensors and (f) proposed NO₂ gas sensing mechanism.

26

Figure 1.10 (a) Heteroatom-containing Ph-COP, Py-COP, and 28 BF-COP organic polymers. (b) Response curves to 40 ppm NH₃ for Ph-COP, Py-COP, and BF-COP sensors. (c) Transient plot illustrating BF-COP sensor response to different concentrations of NH₃, insets showing the correlation between response and concentrations of NH₃. (d) Long-term durability analysis of BF-COP sensor responding to NH₃ (40 ppm) at RT,

xxii

with insets demonstrating the repeatability curve and (e) selectivity of BF-COP sensor against different gases exposed at 40 ppm, with insets showcasing sensor response under varying relative humidity levels.

Figure 1.11 (a) Schematic illustration of growth of NBA–ZnO nanohybrid. (b) Schematic of the flexible sensor and SEM images of interdigitated electrodes. (c) Dynamic response of NBA NPs, ZnO NPs and NBA-ZnO nanohybrid towards 2000 ppm CO₂. (d) Transient response curve of NBA–ZnO nanohybrid towards CO_2 gas (5000 ppm). (e) Selectivity graph of NBA-ZnO nanohybrid towards interfering gases. (f) The dynamic response graph of NBA–ZnO nanohybrid to different concentrations of CO₂ gas. (g) Correlation curve of NBA-ZnO nanohybrid between response and concentration of CO₂ gas and (h) repeatability graph for 3 consecutive cycles to CO_2 (5000 ppm) gas under different bending conditions.

Figure 1.12 (a) Response/recovery times curves to 10 ppm NH₃ for the GCs/PANI-1, GCs/PANI-3, and GCs/PANI-9 sensors. (b) Response of the GCs/PANI-3-based sensor exposed to different concentrations within the range of 5-1600 ppm of NH₃. (c) Repeatability curve of GCs/PANI-3 towards 100 ppm NH₃ for four consecutive cycles. (d) Selectivity graph of GCs/PANI-3 towards 100 ppm of other interfering gases. (e) Impact of RH on the response to NH₃ for GCs/PANI-3. (f) Long-term durability to NH (100 ppm) of GCs/PANI-3 and (g) schematic illustration of the interaction of PANI and NH₃ molecules.

Figure 1.13 (a) Schematic depiction for PAInxAy nanohybrid 34 preparation and sensing device fabrication. (b) Dynamic response of PANI, PAIn10, PAIn20A0.5, PAIn20A1, and PAIn5A2 sensors to different NH₃ concentrations. (c) Single cycle response curve of PAIn20A1 sensor towards 5 ppm NH₃.
(d) Repeatability curve of PANI, PAIn10, PAIn20A0.5,

30

32

PAIn20A1 and PAIn5A2 sensor towards 5 ppm NH₃. (e) Longterm durability graph of PAIn20A1 sensor towards 5 ppm NH₃. (f) Selectivity of PAIn20A1 sensor to NH₃ against different gases and (g) schematic representation of sensing mechanism of PAInx nanohybrid and PAInxAy nanohybrid.

Chapter 2: Investigating the Role of Amide to Thioamide Substitution of a Covalent Organic Polymer for the Selective Chemodetection of H₂S at Room Temperature

Figure 2.1 (a) Schematic representation of COPO synthesis *via* 65 mechanochemical method and gas sensing device fabrication on IDEs. (b) PXRD patterns of 1,3,5-benzenetricarbonyl trichloride, 3,4-diaminobenzhydrazide, COPO and COPS, and (c) FT-IR spectra of 1,3,5-benzenetricarbonyl trichloride, 3,4-diaminobenzhydrazide, COPO and COPS.

Figure 2.2 ¹³C CP-MAS solid-state NMR of (a) COPO and (b)66COPS. Nitrogen (N2) adsorption/desorption isotherm of (c)60COPO and (d) COPS. (inset figures pore diameter curve of60COPO and COPS, respectively, calculated by BJH method).60

Figure 2.3 (a) Thermal stability graph of the COPO and COPS67and (b) DSC curves of COPO and COPS on the second heatingscan.

Figure 2.4 FE-SEM image of (a) COPO and (b) COPS. (c)-(f) 68 EDS pattern and elemental mapping of COPO. (g)-(j) EDS pattern and elemental mapping of COPS.

Figure 2.5 High-resolution TEM images of (a) COPO (inset69SAED pattern) and (b) COPS (inset SAED pattern). AFMimages of (c) COPO and (d) COPS.

Figure 2.6 (a) Single transient response-recovery cycle of the70COPS sensor to 100 ppm H_2S at 25 °C. Transient resistance70response of the (b) COPO and (c) COPS sensors to 100 ppmH_2S at 25 °C.

Figure 2.7 (a) The response of COPO and COPS fabricated 71

sensor towards 100 ppm H₂S. (b) Single transient responserecovery cycle of the COPO towards 100 ppm H₂S. (c) Selectivity of the COPO sensor against other gases at different concentrations. (d) Dynamic response of COPO sensor for H₂S from 100 ppm to 100 ppb. (e) The linear fitting curve of response and concentration of H₂S and (f) effect of RH on sensing performance of COPO towards 100 ppm H₂S. **Figure 2.8** (a) Response of the COPO sensor to 100 ppm H₂S

72

for 25 consecutive cycles at 25 °C and (b) response of the COPO sensor to 100 ppm H_2S for 2 months at 25 °C.

Chapter 3: Tailoring Thiazole Decorated Polymer with Benzoselenadiazole for Enhanced SO₂ Sensing

Figure 3.1 ¹ H NMR spectrum (500 MHz, $CDCl_3$) of 2 .	91
Figure 3.2 ¹³ C NMR spectrum (125 MHz, CDCl ₃) of 2.	91
Figure 3.3 ¹ H NMR spectrum (500 MHz, DMSO- d_6) of 3 .	92
Figure 3.4 13 C NMR spectrum (125 MHz, DMSO- d_6) of 3 .	92
Figure 3.5 ¹ H NMR spectrum (500 MHz, $CDCl_3$) of 5 .	93
Figure 3.6 ¹³ C NMR spectrum (125 MHz, CDCl ₃) of 5.	94
Figure 3.7 ¹ H NMR spectrum (500 MHz, $CDCl_3$) of 6 .	95
Figure 3.8 ¹³ C NMR spectrum (125 MHz, CDCl ₃) of 6.	95
Figure 3.9 (a) PXRD spectrum of 2,5-diaminobenzene-1,4-	99
dithiol, BPBSe and BBTBSe. (b) PXRD spectra of 1,4-	
dicyanobenzene and BBT. (c) FTIR spectrum of 2,5-	
diaminobenzene-1,4-dithiol, BPBSe and BBTBSe and (d)	
FTIR spectra of 2,5-diamino-1,4-benzenedithiol, 1,4-	
dicyanobenzene and BBT.	
Figure 3.10 (a) 13 C CP-MAS NMR of BBTBSe and (b) 1 H	101
NMR (500 MHz, DMSO- <i>d</i> ₆) spectrum of BBT.	
Figure 3.11 N ₂ adsorption/desorption isotherm curves of (a)	102
BPBSe (b) BBTBSe, and (c) BBT (Inset pore diameter curve of	
(a) BPBSe, (b) BBTBSe, and (c) BBT, calculated by NL-DFT	
method). (d) Thermogravimetric analysis of BPBSe and	

BBTBSe and (e) thermogravimetric analysis of BBT to investigate the thermal stability of the curve.

Figure 3.12 FESEM images of (a) BPBSe, (b) BBTBSe.and103(c) BBT. HRTEM images of (d) BBTBSe and (e) BBT.

Figure 3.13 (a) XPS survey spectrum of BBTBSe. The 104 deconvolute spectrum of (b) Se, (c) S 1s, (d) N 1s, and (e) C 1s in BBTBSe. (f) XPS survey spectrum of BBT. The deconvoluted spectrum of (g) S 1s, (g) N 1s, and (i) C 1s present in BBT.

Figure 3.14 Current-Voltage (*I-V*) analysis of (a) BBTBSe and105(b) BBT fabricated sensors.

Figure 3.15 (a) Response of BPBSe, BBT, and BBTBSe 106 sensors to 100 ppm SO₂. (b) Single transient curve of response/recovery time of BBTBSe sensor to 100 ppm SO₂. (c) Selectivity of BBTBSe and BBT sensors for various gases. (d) Dynamic response for BBTBSe and BBT sensors for different concentrations of SO₂ (1 to 100 ppm). (e) The relation between SO₂ concentration (1 to 50 ppm) and the response of BBTBSe sensor and (f) the relation between SO₂ concentration (1 ppm to 50 ppm) and the response of BBT sensor at 25 °C.

Figure 3.16 (a) Response of BBT and BBTBSe sensors 108 towards 100 ppm SO₂ under different RH (57% to 97% RH) conditions. (b) Repeatability curve of BBTBSe and BBT sensor towards SO₂ and (c) long-term stability of BBTBSe and BBT sensors towards 100 ppm SO₂.

Chapter 4: Tailoring NH₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer

Figure 4.1 ¹ H NMR spectrum (500 MHz, $CDCl_3$) of TP3F (3).	129
Figure 4.2 ¹³ C NMR spectrum (125 MHz, CDCl ₃) of TP3F (3).	130
Figure 4.3 (a) Synthetic scheme of conversion of imine based	132
nCOP to amine based nCOP and (b) Schematic illustration of	

fabrication of nCOP on IDE.

Figure 4.4 (a) FTIR spectrum of 3,4-diaminobenzhydrazide, 134 TP3F, nCOPI, and nCOPA. (b) PXRD spectrum of 3,4-diaminobenzhydrazide, TP3F, nCOPI, and nCOPA. (c) ¹³C CP-MAS NMR of COPA. FE-SEM images of as-synthesised (d) nCOPI and (e) nCOPA.

Figure 4.5 FE-SEM images of as-synthesized (a) TP3F, (b) 135 nCOPI and (c) nCOPA. (d)-(i) EDS pattern and elemental mapping of nCOPI. (h)-(k) EDS pattern and elemental mapping of nCOPA. HR-TEM images of (l) nCOPI and (m) nCOPA.

Figure 4.6 Nitrogen sorption isotherm of (a) TP3F, (b) nCOPI, 136 and (c) nCOPA. (d) Thermal stability curve of TP3F, nCOPI, and nCOPA.

Figure 4.7. (a) XPS survey spectrum of nCOPI. Deconvoluted 137 spectra of (b) C1s (c) N1s and (d) O1s of nCOPI. (e) XPS survey spectrum of nCOPA. Deconvoluted spectra of (f) C1s, (g) N1s and (h) O1s of nCOPA.

Figure 4.8 (a) Current-voltage (*I-V*) curve of nCOPA 139 fabricated sensor at 25 °C. (b) Comparison of response for nCOPI and nCOPA towards 500 ppm NH₃ at 25 °C. (c) Single cycle response curve of nCOPA with response/recovery time towards 500 ppm NH₃. (d) Response of nCOPA towards different gases at 100 ppm at 25 °C. (e) Dynamic response curve of nCOPA from 1 to 500 ppm NH₃ concentration at 25 °C. and (f) response of nCOPA towards 500 ppm NH₃ under different humid (57% to 97% RH) condition at 25 °C.

Figure 4.9 (a) Correlation between response of nCOPA and 141 different concentrations of NH_3 (b) Repeatability assessment of nCOPA sensor towards 500 ppm NH_3 for 5 consecutive cycles at 25 °C. (c) Long-term stability curve of nCOPA at every 5th day for 60 days at 25 °C and (d) response of nCOPA to 500 ppm NH_3 at different temperatures.

Chapter 5: Fabricated Chemiresistive Sensor for Detection of Ethanol Using NDICY-ZnO Nanohybrid **Figure 5.1** ¹H NMR spectrum (400 MHz, DMSO- d_6) of 163 Boc-Cap-OH (2). Figure 5.2 ¹³C NMR spectrum (100 MHz, DMSO- d_6) of Boc-163 Cap-OH (2). Figure 5.3 ESI-MS spectrum of Boc-Cap-OH (2). 164 Figure 5.4 ¹H NMR spectrum (400 MHz, DMSO-*d*₆) of Boc-165 Cap-Y-OMe (5). Figure 5.5 ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) of Boc-165 Cap-Y-OMe (5). Figure 5.6 ESI-MS spectrum of Boc-Cap-Y-OMe (5). 166 Figure 5.7 ¹H NMR spectrum (400 MHz, DMSO- d_6) of 167 NDICY-OMe (7). Figure 5.8 13 C NMR spectrum (100 MHz, DMSO- d_6) of 167 NDICY-OMe (7). Figure 5.9 ESI-MS spectrum of NDICY-OMe (7). 168 Figure 5.10 ¹H NMR spectrum (400 MHz, DMSO- d_6) of 169 NDICY (8). Figure 5.11 ¹³C NMR spectrum (100 MHz, DMSO- d_6) of 169 NDICY (8). Figure 5.12 ESI-MS spectrum of the NDICY (8). 169 Figure 5.13 Schematic representations of the synthesis of 170 NDICY-ZnO composite nanohybrid via hydrothermal method and fabrication of nanohybrid on interdigitated electrode. Figure 5.14 Schematic representation of self-assembled 171 organic-inorganic nanohybrid. Figure 5.15 (a) PXRD patterns of NDICY, ZnO, and NDICY-174 ZnO nanohybrid. (b) FTIR spectra of NDICY and NDICY-ZnO nanohybrid. (c) TGA curves of NDICY and NDICY-ZnO and (d) table containing the amount (%) of ZnO in NDICY-ZnO nanohybrid was determined by TGA using the given formula.

Figure 5.16 BET surface area of (a) NDICY, (b) ZnO, and (c) 175 NDICY-ZnO nanohybrid inset with pore diameter curve calculated by NL-DFT method and (d) Table containing BET surface area and pore volume of NDICY, ZnO and NDICY-ZnO nanohybrid.

Figure 5.17 (a) SEM images of NDICY. SEM images of 176 NDICY-ZnO nanohybrids at different molar concentrations (b) 1:25, (c) 1:50 and (d) 1:100 inset with EDS analysis of NDICY-ZnO nanohybrid. (e) Elemental mapping of NDICY-ZnO showing uniform distribution of elements in (a) 1:25, (b) 1:50 and (c) 1:100 molar ratio.

Figure 5.18 (a) SEM image, (b) EDX, (c) and (d) Elemental 177 mapping of ZnO.

Figure 5.19 (a) TEM image of NDICY-ZnO. (b) HRTEM 178 image of NDICY-ZnO. (c) SAED pattern of NDICY-ZnO. (d) TEM of ZnO. (e) HRTEM of ZnO and (f) SAED pattern of ZnO.

Figure 5.20 (a) XPS survey spectra of NDICY-ZnO. 179Deconvoluted XPS spectra for the element of (b) Zn, (c) C1s,(d) O1s, and (e) N1s in NDICY-ZnO nanohybrid.

Figure 5.21 XPS spectra of (a) ZnO. (b) Deconvoluted XPS 180 spectra of (b) Zn and (c) O1s.

Figure 5.22 (a) *I-V* response of NDICY-ZnO nanohybrid at 27 182 °C. (b) Single-cycle response of ethanol when exposed to NDICY, ZnO and NDICY-ZnO sensing layer. (c) Dynamic response-recovery curve of the NDICY-ZnO nanohybrid sensor. (d) Response of ethanol (500 ppm) at different molar concentrations of NDICY and ZnO. (e) Dynamic response of ethanol of the mechanical grinded NDICY-ZnO compositebased sensor to 500 ppm at 27 °C and (f) Response/recovery variation at different concentrations of ethanol vapors.

Figure 5.23 (a) Humidity effect on the sensing layer when 183 ethanol vapors were exposed at 27 °C. (b) The selectivity of

ethanol among different interfering gases and VOCs. (c) The repeatability study of the NDICY-ZnO sensor at 500 ppm of ethanol vapors and (d) long-term stability of ethanol response was studied for 90 days.

Figure 5.24 Reproducibility curve of (a) 1:25, (b) 1:50, and (c)1841:100 NDICY-ZnO based sensors towards 500 ppm ethanol.
LIST OF SCHEMES

Chapter 2: Investigating the Role of Amide to Thioamide					
Substitution of a Covalent Organic Polymer for the					
Selective Chemodetection of H ₂ S at Room Temperature					
Scheme 2.1 Synthetic scheme of COPO and COPS	62				
Scheme 2.2 Interaction of amide and thioamide bonds in the	74				
COPO and COPS with H ₂ S molecules					

Chapter 3: Tailoring Thiazole Decorated Polymer with Benzoselenadiazole for Enhanced SO₂ Sensing

Scheme	3.1	Synthetic	scheme	of	BPBSe	(4,4'-	90
benzo[c][1,2,5]s	elenadiazole-	4,7-diyl)di	benzo	nitrile, 6)		
Scheme 3	5.2 Syn	thetic scheme	e of BBTBS	Se and	l BBT CPs	5	96
Scheme 3	3.3 Sch	ematic repres	sentation of	f fabr	ication of	CPs on	97
an interdi	gitated	electrodes (I	DEs)				
Scheme 3	.4 Inte	raction of BE	BTBSe with	SO ₂	molecules		111

Chapter 4: Tailoring NH₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer

Scheme 4.1 Synthetic scheme for solution phase synthesis 5'- 128 (4-formylphenyl)-[1,1':3',1"-terphenyl]-4,4"-dicarbaldehyde (TP3F), Imine Linkage Nanoporous Covalent Organic Polymer (nCOPI) and Amine Linkage Nanoporous Covalent Organic Polymer (nCOPA)

Scheme 4.2 (a) Schematic representation of sensing 143 mechanism based on electron transfer between the NH₃ (act as electron donor) and p-type nCOPA (electron acceptor, where the majority carriers are holes) and (b) hydrogen bonding between NH₃ gas molecules and nCOPA sensor

Chapter 5: Fabricated Chemiresistive Sensor for Detection

of Ethanol Using NDICY-ZnO Nanohybrid

Scheme 5.1 Overall synthetic pathways for liquid phase 162 synthesis of nucleopeptide

Scheme 5.2 Schematic diagram of the mechanism of ethanol 187 sensing at room temperature when exposed to NDICY-ZnO nanohybrid sensing layer

LIST OF TABLES

5

Chapter 1: General Introduction

Table 1.1 Sources of pollutants, their impact on humanhealth, exposure limit, and the biomarkers for diseasediagnosis

Chapter 2: Investigating the Role of Amide to ThioamideSubstitution of a Covalent Organic Polymer for theSelective Chemodetection of H2S at Room TemperatureTable 2.1 Comparative study of various H2S gas sensors with73COPO

Chapter 3: Tailoring Thiazole Decorated Polymer with Benzoselenadiazole for Enhanced SO₂ Sensing

Table 3.1 Comparison of sensing performance of BBTBSe109sensor with other reported materials towards SO2

Chapter 4: Tailoring NH₃ Sensing Responsiveness through Amine Modification of Imine-based Nanoporous Covalent Organic Polymer

Table 4.1 Comparison of room temperature response of144nCOPA sensor towards NH3 with other reported literature

Chapter 5: Fabricated Chemiresistive Sensor for Detection of Ethanol Using NDICY-ZnO Nanohybrid

Table 5.1 Comparative study of various ethanol gas sensors.186

ACRONYMS

MeOH	Methanol
CO ₂	Carbon Dioxide
TEM	Transmission Electron Microscopy
СО	Carbon Monoxide
NO ₂	Nitrogen Dioxide
NMR	Nuclear Magnetic Resonance
SO ₂	Sulfur Dioxide
H_2S	Hydrogen Disulfide
NaOH	Sodium Hydroxide
NH ₃	Ammonia
K_2CO_3	Potassium Carbonate
EtOAc	Ethyl Acetate
H ₂ O	Water
DMSO	Dimethyl Sulfoxide
HCl	Hydrochloric Acid
HOBt	1-Hydroxybenzotriazole
Y	L-Tyrosine
FT-IR	Fourier Transform Infrared
	Spectroscopy
NDI	Naphthalene Diimide
EDS	Energy Dispersive Spectroscopy
THF	Tetrahydrofuran
Cap	6-Amino Caproic Acid
CDCl ₃	Chloroform-D
Boc	tert-butoxycarbonyl
DCM	Dichloromethane
D	Doublet
SAED	Selected area electron diffraction
t	Triplet
SOCl ₂	Thionyl Chloride
AFM	Atomic Force Microscopy

Na_2SO_4	Sodium Sulphate
XPS	X-ray Photoelectron Microscopy
TLC	Thin Layer Chromatography
IDE	Inter Digitated Electrode
ESI-MS	Electrospray Ionization Mass
	Spectrometry
COP	Covalent Organic Polymer
SEM	Scanning Electron Microscope
СР	Conjugated Polymer
nCOP	Nanoporous covalent organic
	polymer
PXRD	Powder X-ray Diffraction
EtOH	Ethanol
RH	Relative Humidity
TGA	Thermogravimetry Analysis
NaCl	Sodium Chloride
BET	Brunauer-Emmett-Teller
DSC	Differential Scanning Calorimetry
H_2SO_4	Sulphuric Acid
R _g	Resistance in Gas
Ra	Resistance in Air
SD	Standard Deviation

NOMENCLATURES

θ	Angle
ΜΩ	Megaohm
0	Degree
π	Pi
~	Approximately
Å	Angstrom
λ	Wavelength
mM	Millimolar
σ	Slope of the curve
μΜ	Micromolar
μm	Micrometer
GΩ	Gigaohm
nm	Nanometer
%	Percentage
ppm	Parts per million

xxxviii

Chapter 1 General Introduction

Chapter 1

1.1 Introduction

1.1.1 Essential Need for a Gas or Volatile Organic Compound (VOC) Sensor

Over the past few years, the advancement of modern civilization has led to a substantial release of detrimental gases (such as CO₂, NO₂, NH₃, SO₂, and CO) and volatile organic compounds (VOCs) (including ethanol, methanol, acetone, formaldehyde, and chloroform) directly into the air [1,2,3,4,5,6,7,8,9]. The evolution of the contemporary economy, including sectors such as oil, electric power, chemical, and automobile has significantly improved the human productivity and lifestyle. Nevertheless, environmental pollution stemming from these industries cannot be overlooked [9,10,11,12,13]. Many human activities have majorly contributed to environmental pollution for example release of toxic pollutants from different sources such as the burning or dumping of garbage, wastewater treatment, refineries, thermal power plants, automobile emissions, and laboratories (Figure 1.1). Additionally, the agro-livestock sector also contributes to pollution through the release of nutrients, fertilizers, halogenated organic compounds, heavy metals, and plant protection products [1,7].

The constant release of toxic gases or VOCs into the atmosphere, deteriorating our natural surroundings as reported by the United Nations [1,7,14]. According to the World Health Organization (WHO), the toxic gases or VOCs in our environment have led to severe health risks [5,15]. People living in the areas where chemicals and contaminants are exposed without control, experience an elevation in health disease. The continuous intake of these toxic gases or VOCs has an adverse physiological impact on human health for instance queasiness, fainting, long-term illnesses, and respiratory infections which cause early death of large numbers of people [3,8,11,12,14,16]. Moreover, VOCs can be detected in exhaled breath because of diverse metabolic processes within the human body. Remarkably, human breath contains nearly 900 VOCs, serving as biomarkers that aid in the early detection of certain diseases (**Figure 1.1**) [7,3,11,14,16]. The significant permissible limit, properties,

Chapter 1

sources, biomarkers of disease, and negative effects of these toxic gases have been discussed in **Table 1.1**.



Figure 1.1 Sources of dangerous gases or VOCs and their immediate and prolonged impact on human health. [Adapted from google images]

Hence, the rapidly increasing demand for gas or VOC sensors across various applications, including industrial processes, environmental monitoring, healthcare, etc., has sparked considerable research enthusiasm in gas sensor technology. Significant advancement in materials science, gas sensor technology is aiming for major advancements to meet the demands of future sophisticated sensor devices. Additionally, strict government regulation significantly shapes the growth of the gas-sensor market, which is expected to achieve a compound annual growth rate (CAGR) of 7.0%, as stated by market research [17].

The human olfactory system is intricate, highly sensitive, and capable of discriminating a wide range of odors. However, it is important to note that not all gases possess an odor, which makes them undetectable by humans. Additionally, the nasal system may not perceive low concentrations of gases or VOCs. Therefore, there is a significant need to develop user and environment-friendly sensing materials with excellent sensitivity and selectivity for detecting toxic gases or VOCs in real-time. Additionally, sensors with properties such as cost-effective, long self-

life, reliability, rapid response/recovery time, low-temperature operation, tiny, low-power consumption, and low detection limit are in high demand due to their wide range of applications for ecosystem [2,5,10,15,18,19].

Table 1.1 Sources of pollutants, their impact on human health, exposure

 limit, and the biomarkers for disease diagnosis

S.	Gas	Sources	Negative	Exposure	Biomarker	Reference
No.			effects on	limits		
			human	(ppm)		
			health			
1.	H ₂ S	Mining and	Eye and throat	10 ppm	Halitosis	20,21,17
		petroleum	injury,			
		industries	dizziness, loss			
	NO		of sense		A	22.17
2.	NO ₂	Combustion	Chest	<0.2 ppm	Asthma	22,17
		automobiles	coughing			
		nower	damaged			
		plants.	nervous and			
		chemical	cardiovascular			
		factories	systems,			
			respiratory			
			distress			
3.	SO_2	Combustion	Skin and eye	5 ppm	-	17,23
		of fossil	irritation, lung			
		in dustrial	lanure,			
		pollutants	respiratory			
		volcanic	neurological.			
		eruptions,	cardiovascular,			
		power plants	and nervous			
			systems			
4.	NH ₃	Emissions	Respiratory	35 ppm	Hepatic -	24,25,26
		from	tract lesions,		encephal-	
		industry,	damage skin		opathy,	
		agriculture,	and eye,		nelicobacter	
		husbandry	disease		infection	
5.	CO ₂	Burning of	Respiratory	5000 ppm	_	27.28
		fossil fuel,	disorders such			- , -
		volcanic	as asthma and			
		gases	chronic			
			obstructive			
			pulmonary			
6	CO	Incomplete	Nausea	9 ppm	Chronic	17 29 30
0.		combustion	dizziness.	> ppm	obstructi-ve	17,27,30
		industry and	coma		pulmona-ry	
		vehicle			disease	
		emissions,				
		smoking of				
		tobacco		1000		
7.	EtOH	Painting	Eyes and nose	1000 ppm	Fatty liver	31,32
		colors,	irritation,		uiseases	
		of sugar	drowsiness			
I		oi sugar	urowsiness,	1	1	1

Chapter 1

		cooking, and oil refinery	dizziness, nausea			
8.	Acet- one	Vehicle emissions, tobacco smoke	Headache, necrosis, fatigue, and irritation to the eyes, nose, and throat	250 ppm	Diabetic	33,34,35

1.1.2 Types of Gas or VOC Sensors

Gas or VOC sensors are employed in various sectors including environmental surveillance, industrial security, and health care, thus, it is important to detect toxic gases with high selectivity and sensitivity. Therefore, different techniques have been discussed briefly that effectively detect these harmful gases and VOCs (**Figure 1.2**).

1.1.2.1 Resistive Sensor

The principle of resistive sensors is based on alterations in resistance resulting from the adsorption/desorption process of specific gases or VOCs on the surface of the sensing material. Various materials, such as metal oxides, polymers, organic-inorganic hybrid or composites, carbon nanotubes, and graphene, can function as sensing materials. Metal oxides are favored for high-temperature applications, whereas graphene-based metal oxides, polymers, and carbon nanotubes are common in lowtemperature scenarios. The change in resistance, either increasing or decreasing, depends on the targeted gas (reducing or oxidizing) and sensing material type (p- or n-type). The fabrication of these sensors involves placing the sensing layer onto an insulating substrate and positioning them between or on the top of two metal electrodes (for example Au or Pt) to observe the changes in electrical resistance. Resistive gas sensors find utility in detecting toxic and explosive gases or VOCs due to unique characteristics, including easy miniaturization, affordability, excellent sensitivity, simple measuring electronics, and rapid response/recovery time. This versatility makes them vital in various applications where precise gas detection is essential for safety and environmental monitoring [36,37,38,39].

1.1.2.2 Electrochemical Sensor

An electrochemical gas sensor operates on the principle of potential or current changes during the exposure of the gas or VOC on the sensing material. The tested gas or VOC species undergo reduction or oxidation on the cathode or anode, which alters the internal potential or current of the sensing material. Typically, it is composed of a working electrode, reference electrode, and solid electrode, these sensors measure potential changes upon introducing the targeted gas and determines the gas concentration through potential differences. The sensor offers wide-range of gas or VOC detection with high resolution. The electrochemical sensors demonstrate accuracy and repeatability at room temperature, proving a cost-effective and reliable option for gas sensing that also reveals crucial surface chemistry for selective interactions [40].



Figure 1.2 Various kinds of sensors for Gas or VOC detection. [Adapted from ref. no 41,42,43]

1.1.2.3 Colorimetric Sensor

Colorimetric sensors work as a function of change in color due to interaction between sensing material and targeted analyte. Recently, colorimetric tubes have been employed in detecting various toxic gases or VOCs. This technique involves the exposure of gas or VOC through a tube containing a sensing material, where the interaction between the gas and sensing material induces a colour change of the material. The gas concentration is subsequently assessed by measuring the length of the resulting colour stain in the sensing material. Because of its rapid detection, low cost, easy handling, and change in colour, it is regarded as a useful technology for detecting hazardous gases or VOCs. These features make it a practical and accessible option for gas and VOC detection in a variety of applications [40,44,45,46].

1.1.2.4 Optical Sensors

An optical gas sensor functions by detecting a changes in the optical absorption spectrum of the sensitive layer when it adsorbs gas molecules, which provides information about the type and concentration of the gas or VOC. Different techniques like UV, IR, fluorescence, and laser absorption spectroscopy are generally considered as optical sensors. The interaction of the gas molecules and sensing material causes a measurable change in polarity, wavelength, and phase and these changes are employed to recognize and quantify the concentration of gas or VOC. However, the testing equipment for this sensor is typically bulky and costly [40,47,48]. The selection of the sensing technique depends on the targeted analyte, response time, selectivity, cost, and sensitivity requirements.

1.1.3 Sensing Parameters

Analysis of gas or VOC sensing performance is a crucial feature of evaluating the efficiency and reliability of the sensing material and fabricated devices (**Figure 1.3**). Here are some fundamental parameters used for investigating gas or VOC sensing performance:

1.1.3.1 Response: Response is the measure of change in resistance during the exposure of the targeted gas or VOC over the sensing material. This parameter is typically determined as the ratio of change in electrical properties to baseline electrical properties when the targeted

gas or VOC is exposed to the sensing material [50,51,52]. The calculation of the response involves:

$$R (reducing gases) = \frac{R_a}{R_g}$$
(1.1)

$$R (oxidising gases) = \frac{R_g}{R_a}$$
(1.2)

where, R_g and R_a are the measurable properties of the sensor under targeted gas or VOC and in atmospheric air, respectively. Additionally, the percentage of response can be calculated using the given formulas:

$$R(\%) = \frac{R_g - R_a}{R_a} \times 100$$
(1.3)

$$R(\%) = \frac{R_a - R_g}{R_g} \times 100$$
(1.4)



Figure 1.3 Various parameters for gases or VOCs sensing, provide diverse methods to detect and analyze environmental toxic analytes. [Adapted from ref. no 49]

1.1.3.2 Sensitivity: It is described as the ratio of the sensor's response to targeted gas or VOC divided by the concentration per unit [53,54].

$$S = \frac{Response}{Concentration}$$
(1.5)

1.1.3.3 Selectivity: Selectivity is the capacity of the sensing material to discriminate a specific gas or VOC against other interfering gases or VOCs under the same environment [55].

1.1.3.4 Response time: Response time is described as the duration it takes to reach 90% of its total change in the property after the gas or VOC is adsorbed on the sensing material's surface [56,57].

1.1.3.5 Recovery time: The recovery time represents the inverse of the response time. It is defined as the duration it takes to regain 90% of its initial baseline value after the gas or VOC is desorbed from the surface of the sensing material [35,57].

1.1.3.6 Dynamic range: The sensor can detect gas or VOC molecules within the concentration range situated between the lower and the upper concentration limits [13,55,57].

1.1.3.7 Repeatability: The sensing material can induce a consistent response when the same gas or VOC is exposed or removed repeatedly for several consecutive cycles. It assures that the sensor's results remain reliable and robust over a period of time.

1.1.3.8 Stability: It is the capacity of the sensing material to reproduce a similar response without much drift for a longer time when exposed to a specific gas or VOC under the same environment [53,54,58].

1.1.3.9 LOD and LOQ: The limit of detection (LOD) is expressed as the lowest quantity of the targeted gas that can be recognized by the sensing material, while the limit of quantification (LOQ) is expressed as a minimum level of targeted gas that can be quantified accurately and precisely [13,53]. The LOD and LOQ are defined as:

 $LOD = \frac{3 \times SD}{\sigma} \tag{1.6}$

$$LOQ = \frac{10 \times SD}{\sigma} \tag{1.7}$$

where, *SD* is the standard deviation of the response obtained from the calibrated curve and σ is slope of the fitted curve.

Through comprehensive evaluation of sensing parameters, researchers can acquire valuable insights regarding the capabilities and restrictions of the sensing material. This analysis aids in optimizing the sensor's design, pinpointing the area that needs to be modified, and assessing its appropriateness for specific sensing applications.

1.1.4 Sensing Mechanism

The plausible sensing mechanism during the exposure of gases or VOCs into sensing chamber is usually directed by the nature of the sensing material. Therefore, it is important to understand the nature of the material and the interaction of targeted gas with the host material. Herein, the sensing mechanism of the materials has been briefly discussed below.

1.1.4.1 Gas or VOC Sensing Mechanism for Organic-Inorganic Hybrid Material

The sensing mechanism in organic-inorganic hybrids relies heavily on the interaction between the targeted gas or VOC and the sensing material. The hybrids can function as either donors or acceptors of charge carriers, thereby altering the material's resistance based on the predominant charge carriers and the type of the gas or VOC (oxidizing or reducing). Upon exposing the fabricated sensor to the atmosphere, the oxygen molecules present in the air are adsorbed onto the sensing material's surface. These adsorbed oxygen molecules capture electrons (e⁻) from the conduction band of the sensing material, which leads to the formation of oxygen (O) ions on the surface of the sensing material. However, temperature plays a crucial role in the formation of oxygen anions; different oxygen anions are generated at different temperatures (**Equation 1.8-1.11**) [54,59,60,61].

At the optimized temperature, the adsorbed O anions interact with the targeted reducing or oxidizing gas, which leads to the extraction or donation of electrons and results in a subsequent change in the width of the electron depletion layer. This leads to a rise in resistance for n-type material and a reduction in resistance for p-type material [54,60,62,63].

$$O_2(gas) \to O_2(adsorbed) \tag{1.8}$$

$$O_2(adsorbed) + e^- \rightarrow O_2^-(adsorbed) \text{ at } T < 100 \text{ °C}$$
(1.9)

 $O_2^{-}(adsorbed) + e^{-} \rightarrow 20^{-}(adsorbed) \ 100 \ ^{\circ}C < T \ 300 \ ^{\circ}C$ (1.10)

 $O^{-}(adsorbed) + e^{-} \rightarrow O^{2-}(adsorbed) \text{ at } T > 300 \text{ °C}$ (1.11)

The organic-inorganic hybrids are synthesized by combining two distinct materials, facilitating the movement of electrons from a higher to a lower energy state and the migration of holes from a lower energy level to a higher one until the Fermi level attains equilibrium. The type of heterojunction formed at the interface determines the presence of a depletion or accumulation layer (**Figure 1.4a**).



Figure 1.4 The sensing mechanism of n- and p-type (a) organicinorganic hybrid and (b) conjugated polymer or small organic compound toward reducing and oxidizing gases or VOCs.

When the sensor encounters the desired gas or VOC, adsorbed oxygen releases free electrons to the heterojunction. If the metal oxide is of ntype behaviour and the gas or VOC exhibits reducing properties, it has the potential to modify the p-n heterojunctions at the interfaces of the organic-inorganic hybrid. As a result, free electrons are subsequently liberated to the conduction band of the sensing material, which reduces the width of the electron depletion layer. Consequently, the resistance of the sensing material decreases. However, in the presence of oxidizing gases, the gas extracts electrons from the sensing material. As a result, the sensor experiences an expansion in the electron depletion layer and increases the resistance of the sensing material. Conversely, reducing gases or VOCs elevate the resistance in p-type metal oxide due to a decrease in the hole accumulation layer of the hybrid material. Conversely, exposing p-type metal oxide to oxidizing gases reverses this effect and decreases the resistance of the sensing material [61].

Additionally, initial resistance is restored through the desorption process of gas molecules from the material's surface [7,8]. Moreover, the catalytic properties of metal oxide nanoparticles enhance the organic-gas molecule interaction, promoting increased gas adsorption on the nanoparticle surface. This complex interaction demonstrates how the sensor reacts dynamically to various gases, providing insights into its significant behaviour across different gas environments [64,65,66].

1.1.4.2 Gas or VOC Sensing Mechanism for Small Organic Molecules and CP

The fundamental sensing mechanism of small organic molecules and CP remains a mystery. It is widely recognized that small organic molecules or CP can act as either donors or acceptors towards the target gas molecules, which results in a change of the resistance or current in the sensing materials. Gas sensing typically involves two steps; (i) adsorption or physisorption and (ii) charge transfer. These processes alter the charge carrier concentration and resistance by adsorbing target gases or VOCs onto the surface of sensing materials. Moreover, small organic molecules or CPs interact with gases or VOC molecules through weak interactions (i.e. van der Waals interactions or H-bonding), which results in a lower binding energy. During the weak interactions, the gas molecules either donate or attract electrons from the sensing material, which depends upon the type of material (n- or p-type) used, and the

Chapter 1

nature of the targeted gas or VOC (oxidizing or reducing) (**Figure 1.4b**). This process significantly changes the density of the charge carriers and as a result, resistance of the sensing material changes. In both the charge transfer and interaction process, the material recovers to its baseline resistance after the removal of the targeted gas or VOC [45,58,67].

Mishra *et al.* reported the physisorption phenomena to elucidate the dynamic interaction between PCPDTBT sensing film and H₂S molecules. H₂S molecules, known as reductive gas, participate in charge transfer interactions as π electron donors. PCPDTBT, being a p-type organic semiconductor with holes as the majority carriers, plays a crucial role. When H₂S molecules are adsorbed onto the active sites of the PCPDTBT film, they inject electrons into it. These electrons then interact with the majority of holes in the PCPDTBT film, effectively trapping the majority of charge carriers of the sensing film. Consequently, this process reduces carrier density in the PCPDTBT film and increases the resistance of the PCPDTBT film [45].

Trosin *et al.* explained that exposure of NH_3 onto the surface of FNDIbased sensors results in a drastic increment in the IDS current. This was attributed to the transfer of charge from electron-donating NH_3 molecules to electron-deficient n-type semiconductors (FNDI). This charge transfer may induce doping in FNDI, which consequently increases the concentration of charge carriers. Thus, the charge carrier mobility of FNDI enhances and IDS current of FNDI sensor in the presence of NH_3 [46].

However, the main challenges with pure conjugated polymers as host sensing materials are their insufficient sensitivity and poor long-term durability. These limitations can be overcome by functionalizing the backbone of the CP with specific bonds, heteroatomic rings, functional groups, etc. [37].

1.1.5 Functionalized Organic Molecules in Gas or VOC Sensing

Organic molecule or compound-based sensors are gaining significant attention due to their special properties, including diverse materials, costeffectiveness, simple fabrication, selective detection, and room temperature operation. These sensors have shown notable enhancements by optimizing morphology, functionalizing the backbone with specific groups, employing enhanced device structures, etc., which directly tunes the electrical properties of the sensing materials. Thus, the strategic molecular design offers potential for developing a high-performance sensor, which makes these materials feasible for large-scale industrial production [47,68,69,70,71,72].

1.1.5.1 Gas Sensors Based on Small Organic Molecules

Organic small molecules (OSMs) can be broadly categorized as either hole or electron-transporting (p- or n-type) materials, which are determined by the orderly transfer of charge carriers under specific conditions [73]. OSMs including pentacene, rubrene, phthalocyanine, and porphyrin are particularly intriguing due to their extensive π conjugated systems and exceptional optical/electrical characteristics [74]. OSM crystals exhibit weak interactions such as π - π stacking, electrostatic forces, and Van der Waals, which pose a challenge for achieving desired crystal structures through topology-induced synthesis [54,75,76]. Moreover, the charge transport in OSMs relies on carrier hopping between molecules and variations in molecule packing, which affects the semiconducting properties and device performance. Additionally, the extensive efforts have been focused on controlling long-range arrangement of OSMs to influence material or electrical properties, which is crucial for device performance [77,78,79,80]. Smallmolecule semiconducting crystals find applications in solar cells, organic thin-film transistors (OTFT), microfluidic chips, and light-emitting diodes leveraging their unique optical and electronic properties [81]. Despite their advantages in gas or VOC sensors, crystalline OSM-based electronic devices remain infrequently reported, emphasizing their further exploration in electronic devices [82].

Chapter 1



Figure 1.5 (a) Schematic of the fabricated NDI-A device. (b) NDI-A based sensor's response/recovery curve. (c) NDI-A sensor's response to varying NH₃ concentrations. (d) Impact of humidity on NDI-A NH₃ sensing performance. (e) NDI-A sensor's selectivity to NH₃ compared to other gases. (f) Molecular configuration of NDI-CN₄ and NDI-H₄. (g) Device structures of fabricated NDI-CN₄ and NDI-H₄. (h) NH₃ response and recovery times for NDI-CN₄. (i) NDI-CN₄ selectivity against other interfering gases. (j) Dynamic response to NH₃ concentrations from 3 ppm to 50 ppm for NDI-CN₄ sensor and (k) recyclability and long-term durability of NDI-CN₄ sensor toward 50 ppm NH₃. [Adapted from ref. no 86 and 87]

Extensive research has been conducted on naphthalene diimide as OSMs because of their rigid, extensive π -conjugated systems, electron-deficient nature, and intrinsic electroactive imide groups [83,84,85]. Langford *et*

al. broadly studied naphthalene diimide (NDI) based OSMSs, utilizing them for the detection of ammonia (NH₃) at RT. They functionalized the NDI core with phenylalanine and assessed its NH₃ sensing capabilities at RT (Figure 1.5a). The NDI-A sensor exhibited a notable change in current intensity when exposed to different concentrations of NH₃ (range 50–2 ppm). The NDI-A sensor demonstrates high sensitivity (66%) to 50 ppm NH₃ with short response/recovery times (15.3/32 s) (Figure 1.5b) and the lowest detection limit value of 2 ppm (Figure 1.5c). Notably, the sensor displayed a remarkable response in a high-humid environment, showing a 55% response to 50 ppm NH₃ under 90% relative humidity (Figure 1.5d) and exhibited excellent selectivity (Figure 1.5e). The excellent sensing properties of the NDI-A sensor are due to the presence of -COOH groups in NDI-A, which facilitates effective interaction with NH₃ molecules through acid-base interactions and influences the electron transfer process. This alters current or resistance, which was utilized to calculate the NDI-A sensor's response [86]. Further, Langford et al. explored the impact of electron-withdrawing groups (EWG) on sensing performance, when introduced into the NDI moiety. Two derivatives were synthesized, denoted as NDI-CN4 and NDI-H4, and investigated their sensing capabilities for NH₃ gas (Figure 1.5f and 1.5g). The NDI-CN₄ exhibited remarkable sensitivity (178%) to 50 ppm NH₃ at RT compared to NDI-H₄ (0.2%) (Figure 1.5h). The NDI-CN₄ sensor demonstrated rapid response/recovery times (12.5/39 s), exceptional selectivity, linear response with various concentrations, and recyclability (Figure 1.5i-1.5k). Density functional theory (DFT) and cyclic voltammetry analyses suggested that incorporating cyano groups (EWG), significantly lowered the reduction potential of NDI-CN₄, which results in enhanced sensor current due to efficient charge transfer between NH₃ and NDI-CN₄ [87].

In addition, perylene diimide (PDI) has also been widely explored as an organic semiconducting material (OSMS) due to its strong electron affinity, outstanding electron mobility, high absorption coefficient impressive chemical and thermal stability [65,88,89]. Wang *et al.*

investigated the PDI and developed d-THBPDI, in which the imide core was substituted with n-ethylhexamine for detecting hazardous hydrazine vapor (NH₂NH₂) (Figure 1.6a and 1.6b). The d-THBPDI exhibited a 79.4% response ($\Delta R/R_0*100$) with a rapid response/recovery time of 5/5 s to 200 ppm NH₂NH₂ (Figure 1.6c). The sensor demonstrated high selectivity, low reduction potential, reproducibility, and linear response within the concentration range of 5 to 200 ppm (Figure 1.6d-1.6e) [90]. Later, Liu et al. explored the impact of chirality-induced morphology on the sensing performance of PDIs. They synthesized three PDI derivatives, denoted as SOT, STB, and SPP, differing in hydroxyl group position in the alkyl/aryl chains. Among these three derivatives, SPP displayed the highest response (4.5%) with an LOD value of 0.48 ppm and the fastest response/recovery times (17/6 s) than STB and SOT. The reason behind the higher response of SPP is the lowest LUMO energy and uniform films with optimal π - π stacking (3.28 Å). The research highlights the substantial influence of chiral alkyl chains in the bay regions on PDI sensing performance, affecting molecular orbital energy, π - π overlap distance, and crystalline structure [71].



Figure 1.6 (a) Chemical structure of d-THBPDI. (b) An optimized device utilizing d-THBPDI film for gas-sensing measurements. (c) Response/recovery times of d-THBPDI device towards 100 ppm

hydrazine. (d) A device utilizing d-THBPDI film response to hydrazine vapour concentrations ranging from 5 ppm to 200 ppm and (e) repeatability response curve of d-THBPDI to hydrazine vapours. [Adapted from ref. no 90]

The incorporation of pentacene typically increases the charge carrier mobilities (exceeding 1.5 cm²/V) and displays an ambipolar charge transport nature. Additionally, the strategy of functionalization significantly impacts both the electronic and intermolecular ordering characteristics of pentacene [91,92,93,94]. Chi *et al.* presented an exceptionally sensitive chemosensor using a film of TIPS-pentacene for NO₂ detection. The TIPS-pentacene sensor demonstrated responses of 983%, 1833%, 3083%, 4500%, and 5555% to 1, 2, 3, 4, and 5 ppm NO₂, respectively, with a response/recovery time of ~200/400 s. The TIPS-pentacene sensor exhibited reproducibility and selective response to NO₂ over various gases with a calculated LOD value of 20 ppb [95].

Moreover, the modified porphyrin ring plays a crucial role in the electron transfer process and π - π stacking degree, which enhances or weakens their adaptation performance in various applications [96,97,98]. Various groups investigated the semiconducting properties of the material, which can be tuned through interactions with solvents. Xu et al. explored the correlation between the structure of hydrogen bonding, packing mode, and sensing performance in OSMs. The study revealed that hydrogen bonds between porphyrin molecules served as crucial linkage nodes, which influence the long-range crystal packing and establish enduring porosity. They reported three porous OSM based on TCPP, denoted as 1, 2, and 3, showcasing different levels of porosity and π - π interactions among TCPPs by modifying the H-bonding linkage nodes. Compound 1, exhibited extensive overlap between porphyrin rings and robust face-toface π - π interactions, which demonstrates superior sensing performance. Compound 1 exhibited a 37.8 times higher response, and quicker response/recovery times (2.5/0.6 min) compared to compounds 2 and 3 (Figure 1.7a). The TCPP sensor showed a linear increment in response within a range of concentration (0.2 - 100 ppm) with a low LOD value of

20 ppb (Figure 1.7 b). Additionally, it also exhibited robust reproducibility (Figure 1.7c) and exceptional selectivity against 16 interfering gases (Figure 1.7d). This research highlights the effectiveness of hydrogen bonds in shaping and regulating the packing structures of OSM, which improves the pathways for both mass and charge transport (Figure 1.7e) [82].



Figure 1.7 (a) Response of TCPP 1 to 100 ppm NO_2 in dark. (b) Repeatability curve of TCPP 1 towards 100 ppm NO_2 in the visible light. (c) Dynamic response to different concentrations of NO_2 for TCPP 1. (d) Selectivity graph of TCPP 1 to NO_2 against other gases and (e) the possible sensing mechanism for TCPP 1 to NO_2 . [Adapted from ref. no. 82]

Functionalized benzothiophene enhances the intramolecular π - π stacking, boosts charge mobility, reduces π - π distance, improves hole mobility and stability [99,100,101]. Ponomarenko *et al.* explored the formation of monolayer thin films using BTBT organosilicon dimer D2-

Und-BTBT-Hex. They employed Langmuir–Blodgett, Langmuir– Schaefer, and spin-coating methods to achieved uniform and low-defect monolayer. The developed monolayers were utilized in fabricating organic field-effect transistor (OFET) devices, exhibiting outstanding electrical properties with holes mobility of 7×10^{-2} cm² V⁻¹ s⁻¹ at a threshold voltage of near 0 V with on–off ratio of 10⁵. Initial tests indicated that monolayer OFETs displayed an significant response to NH₃ at different concentrations ranging from 400 ppb to 1 ppm, demonstrating that BTBT-based OFETs could be used as a promising material for gas sensing applications on large scale [102].

Despite the widespread application of organic small molecules, they face significant challenges due to their inherent limitations. Specifically, these molecules suffer from poor charge carrier mobility and limited light absorption range. The deposition methods OSM are predominantly vapour-based, which restricts large-scale sensor array manufacturing [54]. Additionally, the polycrystalline nature of OSM microstructures poses challenges in terms of uniformity and flexibility [78]. The key hindrance of OSM-based sensors is their low conductivity, primarily attributed to the mechanism of charge hopping, significantly impeding signal detectability [95]. These shortcomings affect the overall performance of OSM for achieving optimal functionality and efficiency.

1.1.5.2 Gas Sensors Based on Conjugated Polymer

Conjugated polymers (CPs) are semiconductors containing alternate single and double bonds, which form a π -conjugated backbone that enhances the delocalization of electrons. Belonging to the subclass of organic materials, CPs consist of lightweight elements such as H, N, C, and O, which are bonded covalently through sp² hybridized atoms [103,104]. The continuous advancement has sparked the researcher's curiosity, both in industry and academia, leading to a thorough exploration of CP properties and their applications across diverse fields. The outstanding characteristics of CPs, including their lightweight nature, excellent electrical conductivity, tunable band gap, high porosity,

Chapter 1

and enhanced thermal/chemical stability, have facilitated their utilization in various applications such as photovoltaics, OFET, solar cells, biosensors, gas sensors, energy storage, light-emitting diodes and optoelectronics [10,103,104,105]. In contemporary times, the incorporation of various functional groups, bonds, and heteroatomic rings into the backbone of the CPs elevates their development as sensing agents, which contributes to the designing of selective sensor [16].



Figure 1.8 (a) Schematic depiction of the SAPS process for crafting ultrathin nanoporous DPP-DTT films. (b) Responsiveness of DPP-DTT films with different thicknesses to 10 ppm methanol. (c) Comparative bar chart of response and recovery times for different thicknesses of DPP-DTT films. (d) Selectivity curve of bar chart of DPP-DTT films comparing the response/recovery times for 10 ppm MeOH vapour towards different VOCs. (e) Bar chart of DPP-DTT films comparing the response for different VOCs. (f) Dynamic response curve

to diverse concentrations of MeOH. (g) Repeatability curve of DPP-DTT to different VOCs. [Adapted from ref. no 113]

The widespread utilization of nitrogen (N)-rich CP elevates the polymer's basicity and renders them remarkably efficient for detecting acidic gases (H₂S, SO₂, CO₂, etc.) [16]. The incorporation of N atoms into the CP has effectively modulated the energy difference between the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) more efficiently [106,107,108]. Nacify et al., synthesized p(D-co-M) polymer, possessing a moderate level of basicity ideal for detecting a wide range of CO₂ concentration. The p(D-co-M) was employed to design a flexible, low-cost, and reversible CO₂ sensor with chemoresistive properties. The p(D-co-M) sensors exhibited significant decrease in both direct resistance and alternating current impedance across a wide CO_2 concentration range (1–100%) at RT, with response/recovery times of 6/14 min, respectively. When p(D-co-M) was exposed to CO₂ under humid conditions a surface potential increased to +6.34 V, which indicates the protonation of the amine sites and facilitates CO₂ detection under a humid environment. The developed p(D-co-M) sensors demonstrated superior properties, making them promising candidates for flexible, affordable, extremely sensitive, and selective CO₂ sensors, even in elevated humid environment [109].

Amine functionalized polymers can also detect basic gases by engaging in weak interactions, such as hydrogen bonding. Niu *et al.* synthesized four polymers containing N-atom, namely primary amine (1°), secondary amine (2°), tertiary amine (3°), and quaternary ammonium, arranged in distinct configurations to explore their different sensing capabilities. Results revealed that 1°, 2°, and 3° amines served as outstanding NH₃ adsorption sites, showcasing their effectiveness in NH₃ sensing. At RT, the Amino-COP, Caz-COP, and CTF sensors exhibited response values of -62%, -51%, and -76%, respectively, with response/recovery times ranging from 18 to 206 s for 100 ppm NH₃. The LOD values are calculated to be 7.5 ppb, 10 ppb, and 76 ppb for CTF, Amino-COP, and

Chapter 1

Caz-COP, respectively. DFT calculations and in-situ UV-Vis experiments affirmed that 1°, 2°, and 3° amine-containing polymers interact with NH₃ molecules through hydrogen bonding and showed remarkable sensing performance to NH₃ [91].

The incorporation of diketopyrrolo-pyrrole (DPP) involves altering the electronic structure of the backbone and engineering side chains. The backbone of polymer comprising of electron-withdrawing components creates a robust planar structure with significant light absorption property, and enhances their fluorescence brightness [92,110,111,112]. Chang et al. presented a donor-acceptor copolymer DPP-DTT and employed a FET substrate using shearing-assisted phase separation (SAPS) conjugated with selective solvent etching of polystyrene (Figure **1.8a**). This approach fabricates an ultrathin nanoporous structure of DPP-DTT-based OFET device and optimized for gas sensing applications. By adjusting the shear rate, the film morphology achieves an ultrathin thickness and nanopore size of ~ 8 nm and 80 nm, respectively, promoting an effective diffusion of analytes and their interaction with the active sensing layer. Notably, the DPP-DTT OFET sensor (shear coating rate of 4 mm/s) displayed high responsivity to 10 ppm MeOH ($\sim 69.5\%$), with rapid response/recovery times of $\sim 80/234$ s compared to 1 mm/s (40%) and 8 mm/s (35%) (Figure 1.8b-1.8c). Additionally, the device demonstrates outstanding selectivity against other gases or VOCs, linear behaviour with concentration, and repeatability towards different VOCs (Figure 1.8d-1.8g) [113].

The functionalization of benzothiadiazole serves as a fused heterocyclic electron-deficient ring, which is extensively employed in the backbone of polymer for its exceptional intramolecular charge-transfer properties. Consequently, it effectively adjusts the electrical properties and enhances charge transfer capabilities, offering valuable insights for the design of efficient organic sensing materials [97,114,115]. Mishra *et al.* have developed a thin film of PCPDTBT CP, which was utilized as an active sensing layer to detect H_2S at room temperature. The economically viable solution-processed floating film transfer method (FTM) was

adapted to form the PCPDTBT film, followed by solvent vapour annealing to improve the crystallinity. The PCPDTBT film exhibited a response of 71.3% towards 1 ppm H₂S with 8/250 s response/recovery time. The proposed sensing mechanism relies on the interaction between the PCPDTBT film and H₂S gas through a physisorption process. H₂S, a known reductive gas, participates in the charge transfer process as a π electron donor, which injects electrons into the PCPDTBT film (majority carriers are holes) and traps the majority charge carriers, leading to reduced drain current and carrier density. Moreover, the superior planarity, stronger intermolecular interactions, and enhanced conjugation in CPDT and BTD enhance the transport of charge carriers along the backbone of the polymer [67].

Moreover, the incorporation of EWG with fused heterocyclic electrondeficient rings improves the structural and electronic properties of the devices [115]. Noh et al. reported printed sensor based on OTFTs sensitive to NH₃ sensor, which was fabricated with PDFDT polymer. The PDFDT polymer was coated through bar coating and spin coating technique, denoted as BC PDFDT and SC PDFDT, respectively, which omits receptor additives. The OTFT sensors made of 3.1 nm thick BC PDFDT exhibited an 8-fold increase in sensitivity (56%) as compared to the 8.32 nm thick BC PDFDT sensors when exposed to 1 ppm NH₃. The improved response resulted from the significant adsorption of the NH₃ molecules to the bottom surface of the transistor channel in the semiconductor films. PDFDT-NH₃ interactions (weak interactions such as hydrogen bonds and electrostatic interactions) lowered the HOMO levels, which further leads to trapping of holes in PDFDT sensor. These trapped holes transport in the conductive channel of PDFDT and results in a systematic reduction in current when encountered with different NH₃ concentrations. Moreover, DFT calculations demonstrated that incorporation of specific functional (such as fluorine and dithienosilole) groups enhances sensitivity, selectivity and elevates the sensing performance [100].





Figure 1.9 (a) Schematic depiction of flexible NO_2 chemoresistive sensor based on IM-x/P-y CP. (b) Dynamic variations in resistance for IM-0.1/P-y sensors with varied PEI dopant weight ratios. (c) Gas sensitivity was observed when exposed to 0.1-1 ppm NO_2 using IM-0.1/P-y sensors with diverse PEI dopant weight ratios. (d) Selectivity of IM-0.1/P-1.0 sensor toward various gas analytes and humidity. (e) Longterm stability toward cyclic exposure to 1 ppm NO_2 gas for IM-0.1/P-1.0 sensors and (f) proposed NO_2 gas sensing mechanism. [Adapted from ref. no 117]

The presence of imine bonds in the backbone of the polymer tunes the supramolecular assembly between building blocks. Moreover, polyimides containing polymer exhibits electron withdrawing behaviour, excellent mechanical/thermal properties and self-assembly. The strong electron affinity nature tunes the band gap of the polymer and alters the device performance [88,101,116]. Park et al. has developed new PDNIT2/IM-x film doped with poly(ethyleneimine), denoted as IM-x/Py sensing material for detecting NO₂ gas (Figure 1.9a-1.9b). The conjugation in IM-x/P-y was effectively modulated by donating imine bond lone pair electrons to NO₂ analytes and dedoping of PEI dopant, resulting in significant electrical signal changes. The IM-X/P-y film exhibited excellent sensitivity of 240% at 1 ppm NO₂ with LOD value 0.1 ppm (Figure 1.9c). The IM-X/P-y film showed high selectivity factor $(S_{\text{NO2}}/S_{\text{inter}} > 32.2)$ and long term durability (Figure 1.9d and 1.9e). Under NO₂ environment, imine bonds donated its lone pair of electron to NO₂ molecules, which destroys the conjugation in the backbone of the CPs and also decrease the charge carrier density. Consequently, drastic increase in the resistance was observed and response of IM-X/P-y film (Figure 1.9f). Furthermore, IM-x/P-y proved to be a promising flexible sensor platform, capable of monitoring sub-ppm levels of NO₂ gas with high sensitivity even in bent or after 500 bending cycles [117].

Maiti *et al.* synthesized a COP containing imine and amide bonds, which was employed as an effective chemosensor for detecting gaseous H₂S at 25 °C via proton conduction. The fabricated COP sensor achieved a substantial ~51% response towards 200 ppm of H₂S, with an ultrafast response/recovery time of 9/12 s. Moreover, it also demonstrated high selectivity against other gases and response evaluated at different concentrations (50-200 ppm). The adsorption of H₂S at the active sites of the COP restricted the proton transportation process inside the backbone of the COP. Consequently, the resistance of the COP fabricated device enhances and thus, the response of the COP sensor was calculated [118]. The unique feature of triazine moiety for instance presence of the C=N bond and the absence of weak linkage imparts high chemical tunability and stability, high surface area, and porous nature. The nitrogen-rich CPs automatically lead to an extraordinary heteroatom effect (HEA), which enhances the performance of the derived device. The possible reason

could be considerable micron size, non-uniform layered structure, and

large π - π stacking between layers of the CTF material. Yang *et al.* have synthesized triazine decorated 2D polymer (T-2DP) through 2 steps: (i) triflic acid to obtain CTF and (ii) CTF liquid exfoliation to obtain T-2DP. As synthesized polymers were employed as a chemiresistive gas sensor to detect NO₂. The T-2DP sensor showed good response (452.6 ppm^{-1}) at low concentration with 2.2 ppb LOD value. The presence of CTF promotes the transportation and diffusion of the gas molecules, which allows them to interact with maximum active sites of the polymer. Consequently, the interaction of NO₂ molecules with the inner part, inducing modification in the density of the carriers. Moreover, the sensor demonstrated mechanical flexibility, maintaining consistent conductance through 500 bending cycles at 45°, whereas only 2.5% signal was degraded after 1000 cycles, which showcase its excellent strain tolerance. Additionally, the response of T-2DP to NO₂ was observed at various bending angles (0, 30, 45, and 90°). The sensing performance of T-2DP makes it highly suitable for real-time monitoring [119].



Figure 1.10 (a) Heteroatom-containing Ph-COP, Py-COP, and BF-COP organic polymers. (b) Response curves to 40 ppm NH₃ for Ph-COP, Py-COP, and BF-COP sensors. (c) Transient plot illustrating BF-COP sensor response to different concentrations of NH₃, insets showing the correlation between response and concentrations of NH₃. (d) Long-term durability analysis of BF-COP sensor responding to NH₃ (40 ppm) at RT, with insets demonstrating the repeatability curve and (e) selectivity of BF-COP sensor against different gases exposed at 40 ppm, with insets showcasing sensor response under varying relative humidity levels. [Adapted from ref. no 121]
The organic polymers decorated with difluoroboron β -diketones can enhance sensing abilities by adjusting redox property and altering primary charge carriers, thereby improving overall sensing performance [109,120]. Recently, Long *et al.* prepared a range of COPs featuring distinct phenylene (Ph-COP), pyrimidine (Py-COP) or boron β -diketone (BF-COP) units (**Figure 1.10a**). The BF-COP exhibited an outstanding sensing response of 1500 towards 40 ppm NH₃ at RT, which represents the highest response value compared to pristine COPs when utilizing as n-type sensing materials (**Figure 1.10b**). Additionally, the BF-COP exhibited linear increase in the response with increase in concentration, excellent repeatability, long-term durability and selectivity (**Figure 1.10c-10.e**). The incorporation of B/N-heterocyclic groups effectively modifies the electronic interactions, redox properties and charge transfer within typical π -conjugated COPs [121].

1.1.5.3 Gas Sensors Based on Organic-Inorganic Hybrid

The rapid proliferation of organic-inorganic hybrids in both industry and academia has garnered extensive attention in advanced functional material science in recent years. The hybrids composed of organic and inorganic counterparts at nanoscale, engage in molecular-level interactions that generate unique properties at the interface. Organicinorganic hybrid materials serve as a bridge between two domains of chemistry, which makes a significant contribution to the fields of materials science and offers numerous advantages due to their unique features. Inorganic materials within these hybrids can serve multiple roles such as improving mechanical and thermal stability, creating active sites for sensing or catalysts, adjusting the refractive index, specific magnetic, redox, electronic, chemical or electrochemical properties. Incorporating organic components significantly improves mechanical properties, enhances selectivity, and allows the fabrication of films and fibres. Additionally, organic components impart specific chemical or physical properties, which include electrochemical, optical, electrical, etc. behaviour [42,122,123,124].

The collective features of organic-inorganic hybrids arise not solely from the independent qualities of their constituents but also from the synergistic effects generated by the hybrid interface. The characteristics of the inorganic/organic interface, encompassing the surface energy, types of interaction, and the presence of labile bonds, significantly influence various properties such as electrical, chemical, and thermal stability, separation capacity, mechanical, optical, sensing capability, and catalytic activity. Subsequently, these nanocomposites are anticipated to find a wide application in hydrogen storage systems, gas sensors, microwave absorbers, polarizers, and optical limiters [64,125,126,127].



Figure 1.11 (a) Schematic illustration of growth of NBA–ZnO nanohybrid. (b) Schematic of the flexible sensor and SEM images of interdigitated electrodes. (c) Dynamic response of NBA NPs, ZnO NPs, and NBA-ZnO nanohybrid towards 2000 ppm CO_2 . (d) Transient response curve of NBA–ZnO nanohybrid towards CO_2 gas (5000 ppm). (e) Selectivity graph of NBA-ZnO nanohybrid towards interfering gases. (f) The dynamic response graph of NBA–ZnO nanohybrid to different concentrations of CO_2 gas. (g) Correlation curve of NBA-ZnO

nanohybrid between response and concentration of CO_2 gas and (h) repeatability graph for 3 consecutive cycles to CO_2 (5000 ppm) gas under different bending conditions. [Adapted from ref. no 131]

The incorporation of metal oxides into host materials yields several benefits, which include the creation of additional electron depletion layers, increased adsorption sites, enhanced catalytic activity, improved electron transport, and altered energy band structure [37,128,129]. Mukherjee et al. developed a tyrosine functionalized BTC-ZnO nanohybrid using a facile single-pot hydrothermal synthetic route. The Tyr-BTC-ZnO nanohybrid is drop-casted on interdigitated electrodes and employed for the detection of CO at RT. The synthesized nanohybrid exhibited a good response of 94% towards 300 ppm CO and exhibited linear behaviour at different concentrations (5-300 ppm). The synergistic effect of the Try-BTC-ZnO hybrid results in good capacitance behaviour, reduces response time, complete reversibility, and good linearity [130]. Mukherjee et al. delved into the impact of bending on the sensing capabilities of a novel nanohybrid material. They developed a unique hybrid material consisting of NBA (organic component) and ZnO (inorganic component), developed on a flexible polydimethylsiloxane (PDMS) substrate (Figure 1.11a). Figure 1.11b displayed the flexible device and its SEM images. The resulting CO₂ sensor employing NBA-ZnO nanohybrid exhibited remarkable performance, displaying a response of ~9% towards 500 ppm of CO₂ at RT, coupled with a relatively swift response/recovery time of about 3/6 minutes (Figure 1.11c-11d). Moreover, NBA-ZnO nanohybrid exhibited excellent selectivity and linear increase in the response with increase in concentration (Figure 1.11e-11g). The sensor demonstrated excellent mechanical flexibility when subjected to two distinct bending conditions over three consecutive cycles, each with 5000 ppm CO₂ (Figure 1.11h). Under a 20 mm diameter bending condition, the sensor response experienced negligible change (0.8%), while under a 10 mm diameter bending condition, a slight decrease of ~3.53% was observed compared

to the normal (without bending) condition. Further, after reverting the sensor to the normal condition, it retained its properties and exhibited a response of 29.7 % to 5000 ppm of CO_2 [¹³¹].



Figure 1.12 (a) Response/recovery times curves to 10 ppm NH₃ for the GCs/PANI-1, GCs/PANI-3, and GCs/PANI-9 sensors. (b) Response of the GCs/PANI-3-based sensor exposed to different concentrations within the range of 5-1600 ppm of NH₃. (c) Repeatability curve of GCs/PANI-3 towards 100 ppm NH₃ for four consecutive cycles. (d) Selectivity graph of GCs/PANI-3 towards 100 ppm of other interfering gases. (e) Impact of RH on the response to NH₃ for GCs/PANI-3. (f) Long-term durability to NH (100 ppm) of GCs/PANI-3 and (g) schematic illustration of the interaction of PANI and NH₃ molecules. [Adapted from ref. no 132]

The carbon-based materials, predominantly comprising carbon black, graphene, carbon nanotubes, and their derivatives are employed to adjust electronic properties, interface characteristics, and surface durability of the material [132,133,134]. Wang *et al.* engineered 3D hollow graphite capsules-polyaniline (GCs/PANI) hybrid through in-situ polymerization of aniline, adhering it to the graphite surface. The response values recorded for GCs/PANI-1, GCs/PANI-3, and GCs/PANI-9 are 1.14, 1.30, and 1.28 towards 10 ppm NH₃ with response/recovery times of 65/42, 34/42, and 50/52 s, respectively (**Figure 1.12a**). GCs/PANI-3 displayed an increase in response within the concentration range of 5-1600 ppm (**Figure 1.12b**). GCs/PANI-3 demonstrated repeatability behaviour, remarkable selectivity, remarkable response under different humidity, and long-term stability to NH₃ (**Figure 1.12c-1.12f**). The

improved response in detecting NH₃ was ascribed to the synergistic effects of PANI and GCs within the 3D hollow hierarchical hybrid structure (**Figure 1.12g**) [132]. Feng *et al.* reported an extremely sensitive sensor for NH₃ gas based on 2D w-mPPy@rGO heterostructures. The synthesized hetrostructure displays an impressive 45 % response to 10 ppm NH₃, attributed to its substantial specific surface area (193 m²/g). This characteristic ensures rapid gas diffusion and carriers transport. Additionally, w-mPPy@rGO heterostructures displayed remarkable selectivity, superior reversibility, low LOD value (41 ppb), linear behaviour between concentration and response (0.2 to 2 ppm), and excellent repeatability, which offers high potential for practical application [135].

In numerous instances, the introduction of multiple guest materials can mitigate these flaws and significantly enhance sensitivity [20,136,137]. The emergence of organic-inorganic ternary nanocomposites incorporated with single-walled carbon nanohorns (SWCNHs), carbonaceous material, amino acids, metal oxide, and polymer, represents the significant advancement in material research. This development aims to enhance the reliability of the sensors by utilizing the unique properties and contributions of each component in the composite structure [132,138]. Kim et al. reported core-shell nanorod SWCNT@PPy@PA composites synthesized via facile one-pot 0.008 wt% polymerization technique. SWCNT@PPy@PA was employed to detect NH₃ gas, which exhibited a response sensitivity of 2.2 to 1 ppm NH₃ at RT with a response time of 700 s. Notably, the sensor demonstrated reliable detection even at 100 ppb NH₃ concentration at RT, showcasing its potential practical application in gas sensors [139].

The functionalization with noble metals like Pd, Au, Pt, etc. is commonly employed in gas or VOC sensors. The deposition of noble metals onto host materials forms heterostructural nanoparticles, which enhances the sensitivity and lowers the working temperatures through catalytic and adsorption effects [20,59,62]. Lu *et al.* synthesized Au-loaded mesoporous In_2O_3 nanospheres@PANI core-shell nanohybrids (PAInxAy) via hydrothermal and in-situ polymerization methods. They varied the amount of In2O3 and Au-loaded mesoporous In2O3 (2-50 mol%) and compared the sensing performance of PAInxAy. The amount of Au also varied from 0.5% to 2.0% and these materials were fabricated on a flexible polyethylene terephthalate substrate for evaluating the gas sensing performance at RT (Figure 1.13a). The employing PAIn20A1 (1%)Au and 20 mol% sensor, In_2O_3 nanospheres@PANI), demonstrated superior sensing performance with a response value of \sim 46 towards 100 ppm of NH₃. This was approximately 14 times and 4 times greater than the values observed for pure PANI (3.2) and PAIn10 (9.6), respectively at RT. All the fabricated sensors displayed a linear increase in the response with increase in concentration (Figure 1.13b) and PAIn20A1 showed low LOD value of 500 ppb. The PAIn20A1 sensor exhibited rapid response/recovery time (118/144 s -5 ppm) and all the sensors showed excellent repeatability (Figure 1.13c-**1.13d**). In addition, the PAIn20A1 sensor displayed long-term durability with outstanding selectivity (Figure 1.13e and 1.13f). The improved sensing performance resulted from the synergistic effect of p-n junction formed between PANI and mesoporous In₂O₃ nanospheres, which was coupled with the catalytic influence of Au (Figure 1.13g). This sensor holds promise for practical applications in flexible and wearable electronic devices for monitoring and protecting the environment [140].



Figure 1.13 (a) Schematic depiction for PAInxAy nanohybrid preparation and sensing device fabrication. (b) Dynamic response of

PANI, PAIn10, PAIn20A0.5, PAIn20A1, and PAIn5A2 sensors to different NH₃ concentrations. (c) Single cycle response curve of PAIn20A1 sensor towards 5 ppm NH₃. (d) Repeatability curve of PANI, PAIn10, PAIn20A0.5, PAIn20A1 and PAIn5A2 sensor towards 5 ppm NH₃. (e) Long-term durability graph of PAIn20A1 sensor towards 5 ppm NH₃. (f) Selectivity of PAIn20A1 sensor to NH₃ against different gases and (g) schematic representation of sensing mechanism of PAInx nanohybrid and PAInxAy nanohybrid. [Adapted from ref. no 140]

1.2 Summary

This chapter describes the importance of gas sensors. The discussion then expands to encompass various gas sensors, focusing on their ability to detect toxic gases at RT. Sensing parameters, such as response, response time, recovery time, selectivity, dynamic range, sensitivity, LOD, LOQ and stability, are also covered. The sensing mechanisms related to small organic molecules, conjugated polymers, and organicinorganic hybrid materials are described briefly. The chapter emphasize on the significant enhancement of sensing performance through functionalization of the organic materials with different bonds, heteroatomic rings, carbon materials, and metal oxides. The sensing performance of small organic molecules, such as modified NDI, PDI, porphyrin, and pentacene, are also discussed in detail. The chapter also highlights the sensing performance of conjugated polymers, which have been functionalized with imine bonds, amine functional groups, benzothiazole ring, triazine rings, etc. Additionally, the sensing performance of organic-inorganic hybrid materials has also been discussed. The chapter also discusses how the doping of small molecules or polymers with metal oxide, noble metal, carboneous material, etc influences sensing performance. Furthermore, the chapter explores the impact of EWG or EDG on sensing performance when functionalized with the parent material. Also, the chapter delves into the impact of bending on the sensing capabilities of these functionalized materials.

1.3 Thesis Organization

The thesis is organized into six chapters. Chapter 1 offers a succinct review of the current literature, shedding light on the research motivation. It explores existing gas sensors and their operating principles, followed by an in-depth discussion on the functionalization of small organic molecules, conjugated polymers, and organic-inorganic hybrids, evaluating their suitability in gas sensing applications. In Chapter 2, the focus is on designing and synthesizing the amide and thioamide functionalized COP, denoted as COPO and COPS, respectively. Both materials serve as effective gas-sensing agents for detecting H₂S gas in ambient conditions. The chapter details the device fabrication, outlines the setup of a dynamic flow gas sensing system used to assess sensor performance, and delves into the potential mechanism behind gas selectivity. Chapter 3 involves the functionalization of the backbone of a thiazole-based conjugated polymer with а benzoselenadiazole ring, followed by characterization using various techniques. Beyond polymer characterization, the polymers are dropcasted onto interdigitated electrodes (IDEs) for the detection of SO₂ at RT. The chapter also discusses the plausible mechanism based on weak interactions between nitrogen of the heteroatomic rings and SO₂ gas molecules. Then in Chapter 4, we synthesized imine-functionalized COP (COPI), subsequently the imine bonds in COPI were reduced to amine-functionalized COP (COPA) using a reducing agent. COPA and COPI were employed to detect NH₃ in ambient conditions. In addition, the sensing mechanism was proposed on the basis of charge transfer between NH₃ gas molecules and COPA (p-type nature where majority carriers are holes). Chapter 5 involves the development of an organicinorganic nanohybrid material through a facile one-pot hydrothermal method. The study examines how incorporating the inorganic component into the organic component influences sensing performance. This nanohybrid is then utilized for detecting ethanol molecules under ambient conditions. At last, Chapter 6 provides a summary of the current Ph.D. research findings and identifies potential avenues for future exploration. It suggests directions for further research in this field.

1.4 References

- Yadav M., Kumar M., Chaudhary S., Yadav K., Sharma A. (2023), A Review on Chemiresistive Hybrid Zinc Oxide and Nanocomposites for Gas Sensing, Ind. Eng. Chem. Res., 62, 11259–11278 (DOI: 10.1021/acs.iecr.3c00242).
- Verma G., Gokarna A., Kadiri H., Nomenyo K., Lerondel G., Gupta A. (2023), Multiplexed Gas Sensor: Fabrication Strategies, Recent Progress, and Challenges, ACS Sens., 8, 3320–3337 (DOI: 10.1021/acssensors.3c01244).
- (3) Ansari H. R., Mirzaei A., Shokrollahi H., Kumar R., Kim J. Y., Kim H. W., Kumar M., Kim S. S. (2023), Flexible/Wearable Resistive Gas Sensors Based on 2D Materials, J. Mater. Chem. C, 11, 6528–6549 (DOI: 10.1039/d3tc00806a).
- (4) Su H., Yang H., Ma C., Tang J., Zhu C., Wang X., Zeng D. (2023), High Response and Selectivity of the SnO₂ Nanobox Gas Sensor for Ethyl Methyl Carbonate Leakage Detection in a Lithium-Ion Battery, ACS Sens., 9, 444,454 (DOI: 10.1021/acssensors.3c02230).
- (5) Berwal P., Sihag S., Rani S., Kumar A., Jatrana A., Singh P., Dahiya R., Kumar A., Dhillon A., Sanger A., Kumar M., Sharma A., Kumar V. (2023), Hybrid Metal Oxide Nanocomposites for Gas-Sensing Applications: A Review, Ind. Eng. Chem. Res., 62, 14835–14852 (DOI: 10.1021/acs.iecr.3c02288).
- (6) Li X., Sun W., Fu W., Lv H., Zu X., Guo Y., Gibson D., Fu Y. Q. (2023), Advances in Sensing Mechanisms and Micro/Nano structured Sensing Layers for Surface Acoustic Wave-Based Gas Sensors, J. Mater. Chem. A, 11, 9216–9238 (DOI: 10.1039/d2ta10014b).
- (7) Zegebreal L. T., Tegegne N. A., Hone F. G. (2023), Recent Progress in Hybrid Conducting Polymers and Metal Oxide Nanocomposite for Room-Temperature Gas Sensor Applications: A Review, Sensors Actuators A Phys., 359, 114472 (DOI: 10.1016/j.sna.2023.114472).

- (8) Krishna K. G., Umadevi G., Parne S., Pothukanuri N. (2023), Zinc Oxide Based Gas Sensors and Their Derivatives: A Critical Review. J. Mater. Chem. C, 11, 3906–3925 (DOI: 10.1039/d2tc04690c).
- (9) Zhao Y., Liu Y., Han B., Wang M., Wang Q., Zhang Y. N. (2023), Fiber Optic Volatile Organic Compound Gas Sensors: A Review, Coord. Chem. Rev., 493, 215297 (DOI: 10.1016/j.ccr.2023.215297).
- (10) Yang G. G., Kim D. H., Samal S., Choi J., Roh H., Cunin C. E., Lee H. M., Kim S. O., Dincă M., Gumyusenge A. (2023), Polymer-Based Thermally Stable Chemiresistive Sensor for Real-Time Monitoring of NO₂ Gas Emission. ACS Sens., 8, 3687–3692 (DOI: 10.1021/acssensors.3c01530).
- Jo Y. M., Jo Y. K., Lee J. H., Jang H. W., Hwang I. S., Yoo D. J. (2023), MOF-Based Chemiresistive Gas Sensors: Toward New Functionalities, Adv. Mater., 35, 2206842 (DOI: 10.1002/adma.202206842).
- (12) Sharma A., Eadi S. B., Noothalapati H., Otyepka M., Lee H. D., Jayaramulu K. (2024), Porous Materials as Effective Chemiresistive Gas Sensors, Chem. Soc. Rev., 53, 2530-2577 (DOI: 10.1039/d2cs00761d).
- (13) Shinde P. V., Patra A., Rout C. S. (2022), A Review on the Sensing Mechanisms and Recent Developments on Metal Halide-Based Perovskite Gas Sensors, J. Mater. Chem. C, 10, 10196– 10223 (DOI: 10.1039/d2tc01980a).
- (14) Rath R. J., Farajikhah S., Oveissi F., Dehghani F., Naficy S. (2023), Chemiresistive Sensor Arrays for Gas/Volatile Organic Compounds Monitoring: A Review, Adv. Eng. Mater., 25, 2200830 (DOI: 10.1002/adem.202200830).
- (15) Yu H. X., Guo C. Y., Zhang X. F., Xu Y. M., Cheng X. L., Gao S., Huo L. H. (2022), Recent Development of Hierarchical Metal Oxides Based Gas Sensors: From Gas Sensing Performance to Applications, Adv. Sustain. Syst., 6, 2100370 (DOI: 10.1002/adsu.202100370).

- (16) Banga I., Paul A., Poudyal D. C., Muthukumar S., Prasad S. (2023), Recent Advances in Gas Detection Methodologies with a Special Focus on Environmental Sensing and Health Monitoring Applications—A Critical Review, ACS Sens. 8, 3307–3319 (DOI: 10.1021/acssensors.3c00959).
- (17) Mazumder J. T., Jha R. K., Kim H. W., Kim S. S. (2023), Capacitive Toxic Gas Sensors Based on Oxide Composites: A Review, IEEE Sens. J., 23, 17842–17853 (DOI: 10.1109/JSEN.2023.3289835).
- (18) Kumar R., Goel N., Jarwal D. K., Hu Y., Zhang J., Kumar M. (2022), Strategic Review on Chemical Vapor Deposition Technology-Derived 2D Material Nanostructures for Room-Temperature Gas Sensors, J. Mater. Chem. C, 11, 774–801 (DOI: 10.1039/d2tc04188j).
- (19) Liu M., Sun R. Y., Ding Y. L., Wang Q., Song P. (2023), Au/ α -Fe₂O₃/Ti₃C₂T_x MXene Nanosheet Heterojunctions for High-Performance NH₃ Gas Detection at Room Temperature, ACS Appl. Nano Mater., 6, 11856–11867 (DOI: 10.1021/acsanm.3c01744).
- (20) Sharma M., Patel C., Sriram S., Mukherjee S., Das A. K. (2023), Investigating the Role of Amide to Thioamide Substitution of a Covalent Organic Polymer for the Selective Chemodetection of H₂S at Room Temperature, ACS Appl. Polym. Mater.,5, 10065– 10072 (DOI: 10.1021/acsapm.3c01872).
- (21) Luo N., Guo M., Cai H., Li X., Wang X., Cheng Z., Xue Z., Xu J.
 (2023), Engineering a Heterophase Interface by Tailoring the Pt Coverage Density on an Amorphous Ru Surface for Ultrasensitive H₂S Detection, ACS Sensors, 8, 2237–2246 (DOI: 10.1021/acssensors.3c00215).
- (22) Li X., Ge W., Wang P., Zhao H., Tian Y., He X., Liu Z. (2023), SnO₂ Nanosheets for NIR-Enhanced NO₂ Sensing and Adsorption/Desorption, ACS Appl. Nano Mater., 6, 6415-6422 (DOI: 10.1021/acsanm.3c01059.
- (23) Che S., Shou Q., Fan Y., Peng X., Zhou C. S., Fu H., She Y.

(2022), Fluorescent Ionic Liquid Membranes Based on Coumarin for the Real-Time and Visual Detection of Gaseous SO₂, ACS Sustain. Chem. Eng., 10, 2784–2792 (DOI: 10.1021/acssuschemeng.1c08119).

- (24) Chen H., Chen J., Liu Y., Li B., Li H., Zhang X., Lv C., Dong,H.
 (2023), Wearable Dual-Signal NH₃ Sensor with High Sensitivity for Non-Invasive Diagnosis of Chronic Kidney Disease, *Langmuir*, 39, 3420–3430. (DOI: 10.1021/acs.langmuir.2c03347).
- (25) Li P., Xu H., Liu F., Shi J., Gao X., Li J. (2023), Room-Temperature NH₃ Sensors Based on Polyaniline-Assembled Graphitic Carbon Nitride Nanosheets, ACS Appl. Nano Mater., 6, 5145–5154 (DOI: 10.1021/acsanm.2c04940).
- (26) Yuan Y., Zhan G., Peng W., Huang C., Chen H., Lin S. (2023), Trace Ppb-Level NH₃ Sensor Based on Single Petal-like Ce-Doped SnO₂, Mater. Sci. Semicond. Process., 157, 107335 (DOI: 10.1016/j.mssp.2023.107335).
- (27) Davey A. K., Li Z., Lefton N., Leonhardt B. E., Pourghaderi A., McElhany S., Popple D., Dai C., Kahn S., Dods M. N., Zettl A., Carraro C., Maboudian R. (2023), Enhanced ZIF-8-Enabled Colorimetric CO₂ Sensing through Dye-Precursor Synthesis, Sensors Actuators B Chem., 374, 132783 (DOI: 10.1016/j.snb.2022.132783).
- Manzoor S., Talib M., Arsenin A. V., Volkov V. S., Mishra P. (2022), Polyethyleneimine-Starch Functionalization of Single-Walled Carbon Nanotubes for Carbon Dioxide Sensing at Room Temperature, ACS Omega, 8, 893-906 (DOI: 10.1021/acsomega.2c06243).
- (29) Chen B., Li P., Sun L., Wang Y., Wang B. (2022), Co₃O₄ Nanosheets Decorated with In₂O₃ Nanocubes with Exposed {001} Facets for Ppb-Level CO Sensing, ACS Appl. Nano Mater., 5, 11011-11019 (DOI: 10.1021/acsanm.2c02235).
- (30) Qin C., Wang B., Wu N., Han C., Wang Y. (2021), General Strategy to Fabricate Porous Co-Based Bimetallic Metal Oxide Nanosheets for High-Performance CO Sensing, ACS Appl. Mater.

Interfaces, 13, 26318–26329 (DOI: 10.1021/acsami.1c03508).

- (31) Sharma M., Patel C., Maiti S., Mukherjee S., Das A. K. (2023), Fabricated Chemiresistive Sensor for Detection of Ethanol Using NDICY-ZnO Nanohybrid, IEEE Sens. J., 23, 15342–15349 (DOI: 10.1109/JSEN.2023.3276771).
- (32) Kong L., Yuan Z., Gao H., Meng F. (2023), Recent Progress of Gas Sensors Based on Metal Oxide Composites Derived from Bimetallic Metal-Organic Frameworks, TrAC - Trends Anal. Chem., 166, 117199 (DOI: 10.1016/j.trac.2023.117199).
- (33) Gupta M., Verma A., Chaudhary P., Yadav B. C. (2023), MXene and Their Integrated Composite-Based Acetone Sensors for Monitoring of Diabetes, Mater. Adv., 4, 3989–4010 (DOI: 10.1039/d3ma00188a).
- (34) Abbas A., Mansoor S., Nawaz M. H., Chaudhry A. A., Ijaz K., Riaz S., Hayat A. (2023), Growth of Diazonium-Functionalized ZnO Nanoflakes on Flexible Carbon Cloth for Electrochemical Sensing of Acetone in the Liquid Phase, RSC Adv., 13, 11537– 11545 (DOI: 10.1039/d3ra01268a).
- (35) Zheng Z., Jiang N., Liang R., Chi H., Wu J., Jiang J., Ye Z., Zhu
 L. (2023), Enhanced Acetone-Sensing Properties of Pt-Decorated
 In₂O₃ Hollow Microspheres Derived from Pt-Embedded
 Template, Langmuir, 39, 10178–10188 (DOI: 10.1021/acs.langmuir.3c01096).
- (36) Luan S., Hu J., Ma M., Tian J., Liu D., Wang J., Wang J. (2023), The Enhanced Sensing Properties of MOS-Based Resistive Gas Sensors by Au Functionalization: A Review, Dalt. Trans., 52, 8503–8529 (DOI: 10.1039/d3dt01078c).
- (37) Wang Z., Zhu L., Wang J., Zhuang R., Mu P., Wang J., Yan W.
 (2022), Advances in Functional Guest Materials for Resistive Gas Sensors, RSC Adv., 12, 24614–24632 (DOI:10.1039/d2ra04063h).
- (38) Ding Y., Guo X., Zhou Y., He Y., Zang Z. (2022), Copper-Based Metal Oxides for Chemiresistive Gas Sensors, J. Mater. Chem. C, 5, 16218–16246 (DOI: 10.1039/d2tc03583a).
- (39) Mondal B., Gogoi P. K. (2022), Nanoscale Heterostructured

Materials Based on Metal Oxides for a Chemiresistive Gas Sensor, ACS Appl. Electron. Mater., 4, 59–86 (DOI: 10.1021/acsaelm.1c00841).

- (40) Saxena P., Shukla P. (2023), A Review on Recent Developments and Advances in Environmental Gas Sensors to Monitor Toxic Gas Pollutants, Environ. Prog. Sustain. Energy, 42, e14126 (DOI: 10.1002/ep.14126).
- (41) Ma L., Wang L., Chen R., Chang K., Wang S., Hu X., Sun X., Lu Z., Sun H., Guo Q., Jiang M., Hu J. (2016), A Low Cost Compact Measurement System Constructed Using a Smart Electrochemical Sensor for the Real-Time Discrimination of Fruit Ripening, Sensors, 16, 501 (DOI: 10.3390/s16040501).
- (42) Park Y. K., Oh H. J., Bae J. H., Lim J. Y., Lee H. D., Hong S. I., Son H. S., Kim J. H., Lim S. J., Lee W. (2020), Colorimetric Textile Sensor for the Simultaneous Detection of NH₃ and HCl Gases, Polymers, 12, 5157–5174 (DOI: 10.3390/polym12112595).
- (43) Popa D., Udrea F. (2019), Towards Integrated Mid-Infrared Gas Sensors, *Sensors*, 19, 2076 (DOI: 10.3390/s19092076).
- (44) Yuan L., Gao M., Xiang H., Zhou Z., Yu D., Yan R. (2023), A Biomass-Based Colorimetric Sulfur Dioxide Gas Sensor for Smart Packaging, ACS Nano, 17, 6849–6856 (DOI: 10.1021/acsnano.3c00530).
- (45) Li S., Song Y., Xu L., Wang J., Yang Z., Zhao Y., Chen F., Liu B., Liu L., Chen D., Jiao X. (2024), Functional Electrospun Nanofibrous Hybrid Materials for Colorimetric Sensors: A Review, ACS Omega, 9, 5157–5174 (DOI: 10.1021/acsomega.3c08318).
- (46) Yang L., Huangfu C., Wang Y., Qin Y., Qin A., Feng L. (2023), Visual Detection of Mercaptan Gases Using Silver Nanoparticles-Based Colorimetric Sensor Array, ACS Appl. Nano Mater., 6, 22383–22393 (DOI: 10.1021/acsanm.3c04587).
- (47) Paliwal A., Sharma A., Tomar M., Gupta V. (2017), Carbon Monoxide (CO) Optical Gas Sensor Based on ZnO Thin Films, Sensors Actuators, B Chem., 250, 679–685 (DOI:

10.1016/j.snb.2017.05.064).

- (48) Shen Y., Tissot A., Serre C. (2022), Recent Progress on MOF-Based Optical Sensors for VOC Sensing, Chem. Sci., 13, 13978– 14007 (DOI: 10.1039/d2sc04314a).
- (49) Mandal B., Biswas A., Aaryashree, Sharma D. S., Bhardwaj R., Das M., Rahman M. A., Kuriakose S., Bhaskaran M., Sriram S., Than Htay M., Das A. K. Mukherjee S. (2018), π-Conjugated Amine-ZnO Nanohybrids for the Selective Detection of CO2 Gas at Room Temperature, ACS Appl. Nano Mater., 1, 6912–6921 (DOI: 10.1021/acsanm.8b01731).
- (50) Dey A. (2018), Semiconductor Metal Oxide Gas Sensors: A Review, Mater. Sci. Eng. B, 229, 206–217 (DOI: 10.1016/j.mseb.2017.12.036).
- (51) Kumar A., Chen K., Thundat T., Swihart M. T. (2023), Paper-Based Hydrogen Sensors Using Ultrathin Palladium Nanowiresm, ACS Appl. Mater. Interfaces, 15, 5439–5448 (DOI: 10.1021/acsami.2c18825).
- (52) Tai H., Duan Z., Wang Y., Wang S., Jiang Y. (2020), Paper-Based Sensors for Gas, Humidity, and Strain Detections: A Review, ACS Appl. Mater. Interfaces, 12, 31037–31053 (DOI: 10.1021/acsami.0c06435).
- (53) Dai J., Ogbeide O., Macadam N., Sun Q., Yu W., Li Y., Su B. L., Hasan T., Huang X., Huang W. (2020), Printed Gas Sensors. Chem. Soc. Rev., 49, 1756–1789 (DOI: 10.1039/c9cs00459a).
- (54) Mishra R. K., Kumar V., Trung L. G., Choi G. J., Ryu J. W., Bhardwaj R., Kumar P., Singh J., Lee S. H., Gwag J. S. (2023), Recent Advances in ZnO Nanostructure as a Gas-Sensing Element for an Acetone Sensor: A Short Review, Luminescence, 38, 1087– 1101 (DOI: 10.1002/bio.4413).
- (55) Sharma A., Rout C. S. (2021), Advances in Understanding the Gas Sensing Mechanisms Byin Situandoperandospectroscopy. J. Mater. Chem. A, 9, 18175–18207 (DOI: 10.1039/d1ta05054k).
- (56) He K., Jin Z., Chu X., Bi W., Wang W., Wang C., Liu S. (2019), Fast Response-Recovery Time toward Acetone by a Sensor

Prepared with Pd Doped WO₃ Nanosheets, RSC Adv., 9, 28439–28450 (DOI: 10.1039/c9ra04429a).

- (57) Pi W., Chen X., Humayun M., Yuan Y., Dong W., Zhang G., Chen B., Fu Q., Lu Z., Li H., Tang Z., Luo W. (2023), Highly Sensitive Chemiresistive H₂S Detection at Subzero Temperature over the Sb-Doped SnO₂@g-C₃N₄ Heterojunctions under UV Illumination, ACS Appl. Mater. Interfaces, 15,14979–14989 (DOI: 10.1021/acsami.3c00213).
- (58) Bhati V. S., Kumar M., Banerjee R. (2021), Gas Sensing Performance of 2D Nanomaterials/Metal Oxide Nanocomposites: A Review, J. Mater. Chem. C, 9, 8776–8808 (DOI: 10.1039/d1tc01857d).
- (59) Kumar A., Mirzaei A., Lee M. H., Ghahremani Z., Kim T. U., Kim J. Y., Kwoka M., Kumar M., Kim S. S., Kim H. W. (2024), Strategic Review of Gas Sensing Enhancement Ways of 2D Tungsten Disulfide/Selenide-Based Chemiresistive Sensors: Decoration and Composite, J. Mater. Chem. A, 12, 3771–3806 (DOI: 10.1039/d3ta06461a).
- (60) Hassan M., Liang Z., Liu S., Hussain S., Qiao G., Liu G. (2024), Temperature-Driven n- to p-Type Transition of a Chemiresistive NiO/CdS-CdO NO₂ Gas Sensor, Sensors Actuators B Chem., 398, 134755 (DOI: 10.1016/j.snb.2023.134755).
- (61) Kumarage G. W. C., Zappa D., Mihalcea C. G., Maraloiu V. A., Stefan M., Comini E. (2023), Revolutionizing N-Type Co₃O₄ Nanowire for Hydrogen Gas Sensing, Adv. Energy Sustain. Res., 4, 2300067 (DOI: 10.1002/aesr.202300067).
- (62) Majhi S. M., Navale S. T., Mirzaei A., Kim H. W., Kim S. S. (2023), Strategies to Boost Chemiresistive Sensing Performance of In₂O₃-Based Gas Sensors: An Overview, Inorg. Chem. Front., 10, 3428–3467 (DOI: 10.1039/d3qi00099k).
- Murugesan T., Kumar R. R., Anbalagan A. K., Lee C. H., Lin H. N. (2022), Interlinked Polyaniline/ZnO Nanorod Composite for Selective NO₂ Gas Sensing at Room Temperature, ACS Appl. Nano Mater, 5, 4921–4930 (DOI: 10.1021/acsanm.1c04519).

- (64) Kaushik A., Kumar R., Arya S. K., Nair M., Malhotra B. D., Bhansali S. (2015), Organic-Inorganic Hybrid Nanocomposite-Based Gas Sensors for Environmental Monitoring, Chem. Rev., 115, 4571–4606 (DOI: 10.1021/cr400659h).
- (65) Wang N., Tao W., Zhang N., Wang T., Wang X., Liu F., Yan X., Liu F., Liang X., Sun P., Lu G. (2023), Unlocking the Potential of Organic-Inorganic Hybrids in Microwave Gas Sensors: Rapid and Selective NH₃ Sensing at Room-Temperature, Sensors Actuators B Chem., 378, 133112 (DOI: 10.1016/j.snb.2022.133112).
- (66) Dutta P., Gupta G. (2022), Environmental Gas Sensors Based on Electroactive Hybrid Organic-Inorganic Nanocomposites Using Nanostructured Materials, Phys. Chem. Chem. Phys., 24, 28680– 28699 (DOI: 10.1039/d2cp04247a).
- (67) Singh V. K., Verma A., Kumar P., Mishra V. N. (2023), Solution-Processed, Highly-Efficient Organic Field-Effect Transistor Based Hydrogen Sulfide Gas Sensor at Sub-Ppm Regime, IEEE Sens. J., 23, 16600–16607. (DOI: 10.1109/JSEN.2023.3288932).
- (68) Wang C., Dong H., Jiang L., Hu W. (2018), Organic Semiconductor Crystals, Chem. Soc. Rev., 47, 422–500 (DOI: 10.1039/c7cs00490g).
- (69) Zhang Y., Wang Y., Gao C., Ni Z., Zhang X., Hu W., Dong H. (2023), Recent Advances in N-Type and Ambipolar Organic Semiconductors and Their Multi-Functional Applications, Chem. Soc. Rev., 52, 1331–1381 (DOI: 10.1039/d2cs00720g).
- (70) Tang C. G., Hou K., Leong W. L. (2024), The Quest for Air Stability in Organic Semiconductors, Chem. Mater., 36, 28-53 (DOI: 10.1021/acs.chemmater.3c02093).
- (71) Lee G. S., Kwon H. J., An T. K., Kim Y. H. (2023), Current Developments of Eco-Friendly Organic Field-Effect Transistors: From Molecular Engineering of Organic Semiconductors to Greener Device Processing, Chem. Commun., 59, 4995–5015 (DOI: 10.1039/d3cc00191a).
- (72) Bhat V., Callaway C. P., Risko C. (2023), Computational Approaches for Organic Semiconductors: From Chemical and

Physical Understanding to Predicting New Materials, Chem. Rev., 123, 7498–7547 (DOI: 10.1021/acs.chemrev.2c00704).

- (73) Lin Y., Li Y., Zhan X. (2012), Small Molecule Semiconductors for High-Efficiency Organic Photovoltaics, Chem. Soc. Rev., 41, 4245–4272 (DOI: 10.1039/c2cs15313k).
- (74) Sawatzki-Park M., Wang S. J., Kleemann H., Leo K. (2023), Highly Ordered Small Molecule Organic Semiconductor Thin-Films Enabling Complex, High-Performance Multi-Junction Devices, Chem. Rev., 123, 8232–8250 (DOI: 10.1021/acs.chemrev.2c00844).
- (75) Zhan Q., Dai D., Miao F., Wang D., Liu X., Zheng Y. (2023), Bridging the Gap from Single Molecule Properties to Organic Semiconductor Materials, J. Mater. Chem. C, 11, 16117–16124 (DOI: 10.1039/d3tc02462h).
- (76) Trinh C. K., Abdo N. I. (2022), A Mini-Review: Intermolecular Interactions of Small Molecules Containing Amide Groups- Based Organic Semiconductors and Their Applications, J. Mol. Struct., 1269, 133764 (DOI: 10.1016/j.molstruc.2022.133764).
- (77) Asher M., Angerer D., Korobko R., Diskin-Posner Y., Egger D.
 A., Yaffe O. (2020), Anharmonic Lattice Vibrations in Small-Molecule Organic Semiconductors, Adv. Mater., 32, 1908028 (DOI: 10.1002/adma.201908028).
- Wu M., Hou S., Yu X., Yu J. (2020), Recent Progress in Chemical Gas Sensors Based on Organic Thin Film Transistors, J. Mater. Chem. C, 8, 13482–13500 (DOI: 10.1039/d0tc03132a).
- Wang L., Huang W., Li R., Gehrig D., Blom P. W. M., Landfester K., Zhang K. A. I. (2016), Structural Design Principle of Small-Molecule Organic Semiconductors for Metal-Free, Visible-Light-Promoted Photocatalysis, Angew. Chemie Int. Ed., 55, 9783–9787 (DOI: 10.1002/anie.201603789).
- (80) Nitti A., Scagliotti M., Beverina L., Mariucci L., Rapisarda M., Pasini D. (2023), Solution-Processable Thin-Film Transistors from Anthradithiophene (ADT) and Naphthothiopene (NT) Small Molecule-Based p-Type Organic Semiconductors, Mater. Adv., 4,

4590-4597 (DOI: 10.1039/d3ma00552f).

- (81) He Z., Zhang Z., Asare-Yeboah K., Bi S. (2023), Binary Solvent Engineering for Small-Molecular Organic Semiconductor Crystallization, Mater. Adv., 4, 769–786 (DOI: 10.1039/d2ma00726f).
- (82) Deng W. H., He L., Chen E. X., Wang G. E., Ye X. L., Fu Z. H., Lin Q., Xu G. (2022), Crystalline Microporous Small Molecule Semiconductors Based on Porphyrin for High-Performance Chemiresistive Gas Sensing, J. Mater. Chem. A, 10, 12977–12983 (DOI: 10.1039/d1ta10945f).
- (83) Xing F., Li S., Chen L., Dang J. S., He X. (2023), Construction of Naphthalene Diimide Derived Nanostructured Cathodes through Self-Assembly for High-Performance Sodium-Organic Batteries, ACS Nano, 17, 21432–21442 (DOI: 10.1021/acsnano.3c06189).
- (84) Singh V., Kwon S., Choi Y., Ahn S., Kang G., Yi Y., Lim M. H., Seo J., Baik M. H., Byon H. R. (2023), Controlling π–π Interactions of Highly Soluble Naphthalene Diimide Derivatives for Neutral PH Aqueous Redox Flow Batteries, Adv. Mater., 35, 2210859 (DOI: 10.1002/adma.202210859).
- (85) Gámez-Valenzuela S., Torres-Moya I., Sánchez A., Donoso B., López Navarrete J. T., Ruiz Delgado M. C., Prieto P., Ponce Ortiz R. (2023), Extended π-Conjugation and Structural Planarity Effects of Symmetrical D-π-A-π-D Naphthalene and Perylene Diimide Semiconductors on n-Type Electrical Properties, Chem. -A Eur. J., 29, e202301639 (DOI: 10.1002/chem.202301639).
- (86) Ali S., Jameel M. A., Gupta A., Shafiei M., Langford S. J. (2022), A Room Temperature Functioning Ammonia Sensor Utilising a Bis-Phenylalanine Naphthalene Diimide, Sensors Actuators A Phys., 348, 114008 (DOI: 10.1016/j.sna.2022.114008).
- (87) Ali S., Jameel M. A., Oldham G., Gupta A., Shafiei M., Langford S. J. (2022), Enhancement in Room Temperature Ammonia Sensing Properties of Naphthalene Diimides through Core Expansion, J. Mater. Chem. C, 10, 1326–1333 (DOI: 10.1039/d1tc05362k).

- (88) Gautam A., Tiwari J. P. (2024), Recent Advancement of Perylene Diimide as the Electron Acceptor in Organic Solar Cells, J. Mater. Chem. C, 12, 838–853 (DOI: 10.1039/d3tc04054b).
- (89) Li J., Li P., Fan M., Zheng X., Guan J., Yin M. (2022), Chirality of Peryl ene Diimides: Design Strategies and Applications, Angew. Chemie - Int. Ed., 61, e202202532 (DOI: 10.1002/ange.202202532).
- (90) Wang J., He E., Liu X., Yu L., Wang H., Zhang R., Zhang H. (2017), High Performance Hydrazine Vapor Sensor Based on Redox Mechanism of Twisted Perylene Diimide Derivative with Lower Reduction Potential, Sensors Actuators, B Chem., 239, 898–905 (DOI: 10.1016/j.snb.2016.08.090).
- (91) Anthony J. E. (2006), Functionalized Acenes and Heteroacenes for Organic Electronics, Chem. Rev., 106, 5028–5048 (DOI: 10.1021/cr050966z).
- (92) Wu M. X., Li Y., Liu P., Shi X., Kang H., Zhao X. L., Xu L., Li X., Fang J., Fang Z., Cheng Y., Yu H., Shi X., Yang H. B. (2023), Functionalization of Pentacene: A Facile and Versatile Approach to Contorted Polycyclic Aromatic Hydrocarbons, Angew. Chemie Int. Ed., 135, e202309619 (DOI: 10.1002/anie.202309619).
- (93) García-Fernández A., Kammlander B., Riva S., Kühn D., Svanström S., Rensmo H., Cappel U. B. (2023), Interface Energy Alignment between Lead Halide Perovskite Single Crystals and TIPS-Pentacene, Inorg. Chem., 62, 15412–15420 (DOI: 10.1021/acs.inorgchem.3c01482).
- (94) Alanazi F., Eggeman A. S., Stavrou K., Danos A., Monkman A. P., Mendis B. G. (2023), Quantifying Molecular Disorder in Tri-Isopropyl Silane (TIPS) Pentacene Using Variable Coherence Transmission Electron Microscopy, J. Phys. Chem. Lett., 14, 8183–8190 (DOI: 10.1021/acs.jpclett.3c01344).
- (95) Wang Z., Huang L., Zhu X., Zhou X., Chi L. (2017), An Ultrasensitive Organic Semiconductor NO₂ Sensor Based on Crystalline TIPS-Pentacene Films, Adv. Mater., 29, 1703192 (DOI: 10.1002/adma.201703192).

- (96) Xu D., Duan Q., Yu H., Dong W. (2023), Photodynamic Therapy Based on Porphyrin-Based Metal-Organic Frameworks, J. Mater. Chem. B, 11, 5976–5989 (DOI: 10.1039/d2tb02789e).
- (97) Xie M., Liu J., Dai L., Peng H., Xie Y. (2023), Advances and Prospects of Porphyrin Derivatives in the Energy Field, RSC Adv., 13, 24699–24730 (DOI: 10.1039/d3ra04345b).
- (98) Lee H., Park H., Ryu D. Y., Jang W. D. (2023), Porphyrin-Based Supramolecular Polymers, Chem. Soc. Rev., 52, 1947–1974 (DOI: 10.1039/d2cs01066f).
- (99) Tan H., Tan H., Zheng X., Yang J., Yu J., Zhu W. (2020), Significant Influence of the Benzothiophene Ring Substitution Position on the Photovoltaic Performance of Benzodithiophene-Based Donor Polymer, J. Mater. Chem. C, 8, 3183–3191 (DOI: 10.1039/c9tc06594f).
- (100) Morgan D., Yarwood S. J., Barker G. (2021), Recent Developments in C-H Functionalisation of Benzofurans and Benzothiophenes, European J. Org. Chem., 2021, 1072–1102 (DOI: 10.1002/ejoc.202001470).
- (101) Xie P., Liu T., Sun J., Yang J. (2022), Structures, Properties, and Device Applications for [1]Benzothieno[3,2-b]Benzothiophene Derivatives, Adv. Funct. Mater., 32, 2200843 (DOI: 10.1002/adfm.202200843).
- (102) Trul A. A., Sizov A. S., Chekusova V. P., Borshchev O. V., Agina E. V., Shcherbina M. A., Bakirov A. V., Chvalun S. N., Ponomarenko S. A. (2018), Organosilicon Dimer of BTBT as a Perspective Semiconductor Material for Toxic Gas Detection with Monolayer Organic Field-Effect Transistors, J. Mater. Chem. C, 6, 9649–9659 (DOI: 10.1039/C8TC02447B).
- (103) Wang Z., Lin H., Zhang M., Yu W., Zhu C., Wang P., Huang Y., Lv F., Bai H., Wang S. (2023), Water-Soluble Conjugated Polymers for Bioelectronic Systems, Mater. Horizons, 10, 1210– 1233 (DOI: 10.1039/d2mh01520j).
- (104) Yang J., Kang F., Wang X., Zhang Q. (2022), Design Strategies for Improving the Crystallinity of Covalent Organic Frameworks

and Conjugated Polymers: A Review, Mater. Horizons, 9, 121–146 (DOI: 10.039/d1mh00809a).

- (105) Deng J., Zheng L., Ding C., Guo Y., Xie Y., Wang J., Ke Y., Li M., Li L., Janssen R. A. J. (2023), Determinant Role of Solution-State Supramolecular Assembly in Molecular Orientation of Conjugated Polymer Films, Adv. Funct. Mater., 33, 2209195 (DOI: 10.1002/adfm.202209195).
- (106) Sekizkardes A. K., Wang P., Hoffman J., Budhathoki S., Hopkinson D. (2022), Amine-Functionalized Porous Organic Polymers for Carbon Dioxide Capture, Mater. Adv., 3, 6668–6686 (DOI: 10.1039/d2ma00235c).
- (107) Shi Y., Ni R., Zhao Y. (2023), Review on Multidimensional Adsorbents for CO₂ Capture from Ambient Air: Recent Advances and Future Perspectives, Energy and Fuels, 37, 6365–6381 (DOI: 10.1021/acs.energyfuels.3c00381).
- (108) Tong Y., Wang J., Sun Z., Huang W. (2022), Extremely-Long-Lifespan and Ultrahigh-Rate Li-Ion Batteries Using Conjugated Porous Triazine Polymers, ACS Appl. Mater. Interfaces, 15, 14274–14281 (DOI: 10.1021/acsami.2c21851).
- (109) Shahrbabaki Z., Farajikhah S., Ghasemian M. B., Oveissi F., Rath R. J., Yun J., Dehghani F., Naficy S. (2023), A Flexible and Polymer-Based Chemiresistive CO₂ Gas Sensor at Room Temperature, Adv. Mater. Technol., 8, 2201510 (DOI: 10.1002/admt.202201510).
- (110) Yuan T., Xia Q., Wang Z., Li X., Lin H., Mei J., Qian J., Hua J.
 (2023), Promoting the Near-Infrared-II Fluorescence of Diketopyrrolopyrrole-Based Dye for In Vivo Imaging via Donor Engineering, ACS Appl. Mater. Interfaces, 16, 4478–4492 (DOI: 10.1021/acsami.3c16784).
- (111) Mukhopadhyaya T., Wagner J., Lee T. D., Ganley C., Tanwar S., Raj P., Li L., Song, Y., Melvin S. J., Ji Y., Clancy P., Barman I., Thon S., Klausen R. S., Katz H. E. (2023), Solution-Doped Donor–Acceptor Copolymers Based on Diketopyrrolopyrrole and 3, 3'-Bis (2-(2-(2-Methoxyethoxy) Ethoxy) Ethoxy)-2, 2'-

Bithiophene Exhibiting Outstanding Thermoelectric Power Factors with p-Dopants, Adv. Funct. Mater., 34, 2309646 (DOI: 10.1002/adfm.202309646.

- (112) Qi F., Feng H., Peng Y., Jiang L., Zeng L., Huang L. (2024), New Type Annihilator of π-Expanded Diketopyrrolopyrrole for Robust Photostable NIR-Excitable Triplet–Triplet Annihilation Upconversion, ACS Appl. Mater. Interfaces, 16, 7512-7521 (DOI: 10.1021/acsami.3c17679).
- (113) Tran V. V., Jeong G., Wi E., Lee D., Chang M. (2023), Design and Fabrication of Ultrathin Nanoporous Donor-Acceptor Copolymer-Based Organic Field-Effect Transistors for Enhanced VOC Sensing Performance, ACS Appl. Mater. Interfaces, 15, 21270–21283 (DOI: 10.1021/acsami.3c00105).
- (114) Zhu X. Z., Hu H. D., Chen S. H., Li, Y. M., Yan, J. F., Yuan Y. F.
 (2023), Nonlinear Properties of Benzothiadiazole-Based Intramolecular Charge-Transfer Compounds, New J. Chem., 47, 4299–4305 (DOI: 10.1039/d2nj06157k).
- (115) Zaier R., Martel A., Antosiewicz T. J. (2023), Effect of Benzothiadiazole-Based π-Spacers on Fine-Tuning of Optoelectronic Properties of Oligothiophene-Core Donor Materials for Efficient Organic Solar Cells: A DFT Study, J. Phys. Chem. A, 127, 10555-10569 (DOI: 10.1021/acs.jpca.3c04866).
- (116) Kim T., Park B., Lee K. M., Joo S. H., Kang M. S., Yoo W. C., Kwak S. K., Kim B. S. (2018), Hydrothermal Synthesis of Composition- and Morphology-Tunable Polyimide-Based Microparticles, ACS Macro Lett., 7, 1480–1485 (DOI: 10.1021/acsmacrolett.8b00680).
- (117) Park H., Kim D. H., Ma B. S., Shin E., Kim Y., Kim T. S., Kim F. S., Kim I. D., Kim B. J. (2022), High-Performance, Flexible NO₂ Chemiresistors Achieved by Design of Imine-Incorporated n-Type Conjugated Polymers, Adv. Sci. , 9, 2200270 (DOI: 10.1002/advs.202200270).
- (118) Xu H., Li J., Fu Y., Li P., Luo W., Tian Y. (2020), A Covalent Organic Polymer as an Efficient Chemosensor for Highly

Selective H₂S Detection through Proton Conduction, ACS Appl. Nano Mater., 3, 8075–8087 (DOI: 10.1021/acsanm.0c01533).

- (119) Yang K., Yuan W., Hua Z., Tang Y., Yin F., Xia D. (2020), Triazine-Based Two-Dimensional Organic Polymer for Selective NO₂ Sensing with Excellent Performance, ACS Appl. Mater. Interfaces, 12, 3919–3927 (DOI: 10.1021/acsami.9b17450).
- (120) Poon C. T., Wu D., Lam W. H., Yam V. W. W. (2015), A Solution-Processable Donor-Acceptor Compound Containing Boron(III) Centers for Small-Molecule-Based High-Performance Ternary Electronic Memory Devices, Angew. Chemie - Int. Ed., 54, 10569–10573 (DOI: 10.1002/anie.201504997).
- (121) Song W., Sun J., Wang Q., Wu H., Zheng K., Wang B., Wang Z., Long X. (2023), N-Type Boron β-Diketone-Containing Conjugated Polymers for High-Performance Room Temperature Ammonia Sensors. Mater. Horizons, 11, 1023–1031 (DOI: 10.1039/d3mh01596c).
- (122) Mir S. H., Nagahara A., Thundat T., Mokarian-tabari P., Furukawa H., Khosla A. (2018), Review — Organic-Inorganic Hybrid Functional Materials : An Integrated Platform for Applied Technologies, J. Electrochem. Soc., 165, B3137 (DOI: 10.1149/2.0191808jes).
- (123) Arora S., Nagpal R., Gusain M., Singh B., Pan Y., Yadav D., Ahmed I., Kumar V., Parshad B. (2023), Organic-Inorganic Porphyrinoid Frameworks for Biomolecule Sensing, ACS Sensor, 8, 443–464 (DOI: 10.1021/acssensors.2c02408).
- (124) Yoshioka D., Yoneda Y., Chang I. Y., Kuramochi H., Hyeon-Deuk K., Kobayashi Y. (2023), Quasi-Reversible Photoinduced Displacement of Aromatic Ligands from Semiconductor Nanocrystals, ACS Nano, 17, 11309–11317 (DOI: 10.1021/acsnano.2c12578).
- (125) Wang S., Kang Y., Wang L., Zhang H., Wang Y., Wang Y.
 (2013), Organic/Inorganic Hybrid Sensors: A Review, Sensors Actuators, B Chem., 182, 467–481 (DOI: 10.1016/j.snb.2013.03.042).

- (126) Zhang F., Sherrell P. C., Luo W., Chen J., Li W., Yang J., Zhu M.
 (2021), Organic/Inorganic Hybrid Fibers: Controllable Architectures for Electrochemical Energy Applications, Adv. Sci., 8, 2102859 (DOI: 10.1002/advs.202102859).
- (127) Li S., Zhang M., Dong Y., Gao J., Cheng P., Wang H. (2023), Density Functional Theory Study of P-Doped Co₃O₄ (111) Facets for HCHO Adsorption: Implications for Metal Oxide Semiconductor Gas Sensors, ACS Appl. Nano Mater., 6, 17501– 17511 (DOI: 10.1021/acsanm.3c02656).
- (128) Jasper I., Valério T. L., Klobukoski V., Pesqueira C. M., Massaneiro J., Camargo L. P., Dall' Antonia L. H., Vidotti M. (2023), Electrocatalytic and Photoelectrocatalytic Sensors Based on Organic, Inorganic, and Hybrid Materials: A Review, Chemosensors, 11, 261 (DOI: 10.3390/chemosensors11050261).
- (129) Ma S., Xu J. (2023), Nanostructured Metal Oxide Heterojunctions for Chemiresistive Gas Sensors, J. Mater. Chem. A, 11, 23742– 23771 (DOI: 10.1039/d3ta04953a).
- (130) Aaryashree A., Mandal B., Biswas A., Bhardwaj R., Agarwal A., Das A. K., Mukherjee S. (2021), Mesoporous Tyrosine Functionalized BTC-ZnO Composite for Highly Selective Capacitive CO Sensor, IEEE Sens. J., 21, 2610–2617 (DOI: 10.1109/JSEN.2020.3027786).
- (131) Mandal B., Biswas A., Aaryashree, Sharma D. S., Bhardwaj R., Das M., Rahman M. A., Kuriakose S., Bhaskaran M., Sriram S., Than Htay M., Das A. K. Mukherjee S. (2018), π-Conjugated Amine-ZnO Nanohybrids for the Selective Detection of CO₂ Gas at Room Temperature, ACS Appl. Nano Mater., 1, 6912–6921 (DOI: 10.1021/acsanm.8b01731).
- (132) Wang H., Nie S., Li H., Ali R., Fu J., Xiong H., Li J., Wu Z., Lau W. M., Mahmood N., Jia R., Liu Y., Jian X. (2019), 3D Hollow Quasi-Graphite Capsules/Polyaniline Hybrid with a High Performance for Room-Temperature Ammonia Gas Sensors, ACS Sensors, 4, 2343–2350 (DOI: 10.1021/acssensors.9b00882).
- (133) Wang X., Ugur A., Goktas H., Chen N., Wang M., Lachman N.,

Kalfon-Cohen E., Fang W., Wardle B. L., Gleason K. K. (2016), Room Temperature Resistive Volatile Organic Compound Sensing Materials Based on a Hybrid Structure of Vertically Aligned Carbon Nanotubes and Conformal OCVD/ICVD Polymer Coatings, ACS Sensors, 1, 374–383 (DOI: 10.1021/acssensors.5b00208).

- (134) Yang Z., Zhang Y., Gao S., Zhao L., Fei T., Liu S., Zhang T.
 (2021), Hydrogen Bonds-Induced Room-Temperature Detection of DMMP Based on Polypyrrole-Reduced Graphene Oxide Hybrids, Sensors Actuators B Chem., 346, 130518 (DOI: 10.1016/j.snb.2021.130518).
- (135) Gao J., Qin J., Chang J., Liu H., Wu Z. S., Feng L. (2020), NH₃
 Sensor Based on 2D Wormlike Polypyrrole/Graphene Heterostructures for a Self-Powered Integrated System, ACS Appl. Mater. Interfaces, 12, 38674–38681 (DOI: 10.1021/acsami.0c10794).
- (136) Jiang R., Baker D. R., Tran D. T., Li J., Leff A. C., Zhang S. S.
 (2020), Multimetallic FeCoNiOx Nanoparticles Covered with Nitrogen-Doped Graphene Layers as Trifunctional Catalysts for Hydrogen Evolution and Oxygen Reduction and Evolution, ACS Appl. Nano Mater., 3, 7119–7129 (DOI: 10.1021/acsanm.0c01434).
- (137) Xu Y., Gao L., Zhou Y. (2022), Synthesis of Trifunctional Inorganic/Organic Hybrid Nanocomposites and Their Applications for Recognition and Elimination of Heavy Metal Ions, Appl. Surf. Sci., 605, 154659 (DOI: 10.1016/j.apsusc.2022.154659).
- (138) Kumar J. S., Bolar S., Murmu N. C., Ganesh R. S., Inokawa H., Banerjee A., Kuila T. (2019), Synthesis of Tri-Functional Core-Shell CuO@carbon Quantum Dots@carbon Hollow Nanospheres Heterostructure for Non-Enzymatic H₂O₂ Sensing and Overall Water Splitting Applications, Electroanalysis, 31, 2120–2129 (DOI: 10.1002/elan.201900226).
- (139) Xuan Du W., Lee H. J., Byeon J. H., Kim J. S., Cho K. S., Kang

S., Takada M., Kim J. Y. (2020), Highly Sensitive Single-Walled Carbon Nanotube/Polypyrrole/Phenylalanine Core-Shell Nanorods for Ammonia Gas Sensing, J. Mater. Chem. C, 8, 15609–15615 (DOI: 10.1039/d0tc04335d).

(140) Li S., Diao Y., Yang Z., He J., Wang J., Liu C., Liu F., Lu H., Yan X., Sun P., Lu G. (2018), Enhanced Room Temperature Gas Sensor Based on Au-Loaded Mesoporous In₂O₃ Nanospheres@ polyaniline Core-Shell Nanohybrid Assembled on Flexible PET Substrate for NH₃ Detection, Sensors Actuators, B Chem., 276 526–533 (DOI: 10.1016/j.snb.2018.08.120).

Chapter 2 Investigating the Role of Amide to Thioamide Substitution of a Covalent Organic Polymer for the Selective Chemodetection of H₂S at Room Temperature

2.1 Introduction

Hydrogen sulfide (H₂S) is a colorless, combustible, highly toxic, and corrosive gas with a rotten egg-like odor. It can harm the nervous system of human beings even at low concentrations [1,2]. H₂S is often generated from natural gas processing, coal gasification plants, laboratories, sewage, petroleum extraction, food processing plants, and the degradation of sulfur-rich foods [2,3,4]. According to the American Conference of Governmental Industrial Hygienists (ACGIH) and the Occupational Safety and Health Administration (a Federal organization in the US), exposure to 10 ppm of H₂S is permissible for 8 h.⁴ Therefore, it is important to design and develop gas sensors that can effectively and selectively detect H₂S gas at parts per million and subppm levels. Various types of gas sensors, such as chemiresistive, electrochemical, optical, and fluorescent gas sensors, have been explored to detect toxic and harmful gases [5,6]. Among these, chemiresistive sensors have gained significant interest due to their low cost, long-term stability, easy fabrication, repeatability, real-time response, and ease of miniaturization [4,7,8].

Currently, sensors based on metal oxide are used to detect toxic gases at parts per million and subppm levels. However, these sensors have limitations such as the need for high-temperature operation and lack of selectivity [9,10]. Choa *et al.* have reported a sensor based on SnO₂–CuO nanotubes for detecting H₂S, which operates at 200 °C [11]. Therefore, scientists are looking for a different class of organic material that exhibits high selectivity and can operate at room temperature [9]. Recently, there has been significant interest in the development of porous materials such as covalent organic frameworks (COF), metal–organic frameworks (MOFs), porous carbons (PCs), and covalent organic polymers (COPs) due to their various potential applications [12]. Among the aforementioned materials, COPs formed from strong covalent bonds containing hetero atoms such as C, N, O, and S are considered more promising. This is due to their high tunable porosity, low mass density, large surface area, high chemical, and thermal stability, and long-term

durability [13,14,15,16]. COPs have a wide range of applications in energy storage, gas sensing, gas storage, dye degradation, and catalysis [17,18,12,19,20,21]. Various chemical reactions have been studied for the synthesis of COPs, such as condensation and coupling methods. These methods involve drastic conditions like high temperature, inert atmosphere, and controlled pressure [22]. Therefore. the mechanochemical method is used as a promising alternative route to synthesize COPs. This is because the grinding action provides the initiation energy for the reaction to start, increases the active sites, and enhances the reactivity of precursors [23]. Furthermore, mechanochemical synthesis minimizes the use of solvents, reduces reaction time, operates at room temperature, and produces structural and electronic defects that enhance selectivity [24,25,26]. Rajput et al. have used a mechanochemical method to synthesize a porous polymer framework 1,3,5-benzenetricarbonyl trichloride using and рphenylenediamine or benzidine (BD) [27]. In particular, polyamide COP is well known for its excellent thermal, mechanical, and chemical stability. The COP with amide bonds increases basicity, which can be utilized for detecting acidic gases [28,29]. Thioamide is formed by replacing oxygen (C=O) in the amide bond with sulfur (C=S). Thioamide-based compounds can adjust binding affinity or conformational flexibility through hydrogen bonding [30] Moreover, thioamides impart different strengths of H-bonding compared to amides, and the sulfur in thioamides acts as a Lewis base [31]. The presence of sulfur in the thioamide bond increases the rotational barrier at the C-N bond and decreases the capacity to accept hydrogen, but increases the capacity to donate hydrogen compared to an amide bond [32]. These points motivated us to synthesize a covalent organic polymer with abundant amide and thioamide bonds using mechanochemical and solution phase methods. These polymers have been used as sensing materials for the detection of H₂S gas under ambient conditions. In this study, we have synthesized COPO and COPS polymers using mechanochemical and solution phase methods, respectively. The sensor based on COPO shows a better response to H_2S gas compared to the

sensor based on COPS 25 °C. The response of COPO to H_2S was also studied (i) in relation to other interfering gases, (ii) different concentrations of H_2S , and (iii) varying levels of humidity. Here, a solvent-free method was used to synthesize COPO, resulting in selective and highly sensitive detection of H_2S gas with complete recovery.

2.2 Aims and Objectives

The aims and objectives of the current work are mentioned as follows;

- (i) To synthesize an amide-decorated covalent organic polymer(COPO) and further, amide bonds were converted to thioamide bonds in the COP.
- (ii) To investigate the presence of amide and thioamide bonds in COPO and COPS, respectively.
- (iii) To evaluate the thermal stability and surface morphology of the COPO and COPS.
- (iv) To investigate the sensing performance of COPO and COPS for detecting H₂S at RT.
- (v) To investigate the selectivity, the dynamic response at different concentrations, and the effect of humidity on the sensing response of COPO.
- (vi) To investigate the proposed sensing mechanism of the COPO sensor.

2.3 Experimental Section

2.3.1 Materials and Methods

1,3,5-Benzenetricarbonyl trichloride, 3,4-diaminobenzhydrazide, triethylamine, ethanol, and ethyl acetate were purchased commercially.

2.3.2 Synthesis of COPO and COPS

The COPO was synthesized using an environmentally friendly mechanochemical method at ambient conditions [27] In a typical mechanochemical technique, 1,3,5-benzenetricarbonyl trichloride (1 g) and 3,4-diaminobenzhydrazide (640 mg) were taken in a mortar and a few drops (4 to 5 drops) of triethylamine (TEA) were added to neutralize

the hydrochloric acid (HCl) that would be released during the reaction. Within 1 min, it turned into a pale brown thick paste. Then, it was manually ground with a pestle until it became a fine powder. The resulting powder was washed with water, ethanol, and ethyl acetate to remove HCl, TEA, and any unreacted precursors. It was then dried in an oven at 70 °C for 10 h to remove any remaining water, ethanol, and ethyl acetate, resulting in a faded brown amide-decorated COP (**Figure 2.1a**). The COPO was dispersed in degassed tetrahydrofuran and stirred for 10 min. Then, a solution of Lawesson's reagent in degassed THF was added to the mixture. The reaction was heated to 90 °C and refluxed for 5 days under an argon atmosphere. After that, the reaction mixture was cooled, filtered, washed, and dried in an oven at 60 °C for 10 h to obtain white solid powder (**Scheme 2.1**).





2.3.3 Characterization of COPO and COPS

Solid-state Cross-Polarization Magic Angle Spinning Carbon-13 Nuclear Magnetic Resonance (¹³C CP-MAS NMR spectrum) spectrum was recorded using a solid-state NMR spectrometer (JEOL, model: ECZ600R/S1; proton frequency: 600 MHz). Powered X-ray Diffraction (PXRD) data was collected using Rigaku SmartLab, an Automated Multipurpose X-ray Diffractometer. Fourier transform infrared (FT-IR) spectra of polyamide COP were recorded on a Bruker (Tensor-27) FT-IR spectrophotometer. Thermogravimetric analysis (TGA) was obtained by using a Mettler Toledo Thermal Analyzer with a heating rate of 10 °C/min and heated from 25 to 800 °C under a nitrogen atmosphere.

Differential Scanning Calorimetry (DSC) analysis was performed on (model: I PerkinElmer DSC 8000) with a heating rate of 10 °C/min and heated from 25 to 500 °C. Surface area analysis was recorded using Quantachrome, Autosorb iQ2. In addition, the pore size was obtained by using Barrette-Joyner-Halenda (BJH) method. For field emission scanning electron microscopy (FE-SEM) analysis, a small quantity of COP was dispersed in ethanol and drop-casted on a glass slip. Then, the glass slip was dried in an oven and coated with Au. High-resolution transmission electron microscopy (HR-TEM) analysis was performed using a Field Emission Gun-Transmission Electron Microscope 200 kV (model no. Tecnai G2, F30), operated on a voltage of 200 kV. Atomic force microscopy (AFM) analysis was examined on park systems NX10 and the samples were prepared on mica foil.

2.3.4 H₂S Sensor Fabrication

2.3.4.1 Device dimensions: The platinum IDEs are patterned on Corning glass using photolithography with a 5214 E image reversal photoresist. The electrodes have a thickness of 200 nm, with a spacing of 25 μ m between them. To enhance adhesion, a 20 nm titanium layer is deposited via e-beam evaporation at room temperature, under a working pressure of 1.5 × 10⁻⁷ Torr and a deposition rate of 0.3 Å/s. Additionally, the contact pads on the device are also made up of same material as that of electrodes (i.e., platinum) and the dimensions of the contact pads are 1mm × 1mm.

2.3.4.2 Device fabrication: The resulting powder of COPO and COPS was mixed with 3 to 4 droplets of water to form a uniform thick paste and drop-casted on the interdigitated electrode (IDE) to form a uniform layer. The fabricated device was annealed at 80 °C in a hot air oven for 12 h.

2.3.4.3 Sensing setup and measurements: The sensing experiment was performed in a dynamic flow-through measurement system, which includes a stainless steel chamber with an internal volume of approximately 500 cm³. The sensor's contact pads were connected to the Keithley 2612A source meter, which was used to observe the change in

the resistance during exposure or removal of the targeted gas. The flow rate of the H₂S was controlled by a mass flow controller, MFC (model: Alicat®, MC 1slpm, USA) [33]. The COPO and COPS fabricated devices were placed in the sensing chamber for gas sensing experiment. The electrical resistance of the sensor was measured using Keithley source meter. During the gas sensing experiment, a fixed current of 10 μ A was set. The response % of sensing material when exposed to a targeted gas is defined as

$$\frac{R_g - R_a}{R_a} \times 100 \tag{2.1}$$

where, R_{gas} and R_{air} are the resistance in targeted gas and air, respectively. Generally, response time is expressed as the experiment time taken by the sensing material to reach 90% of the total resistance change after exposing the target gas. Similarly, recovery is defined as the time taken by the sensing material to come back to 90% to its base resistance [34].

The cylinders of H₂S, SO₂, CO₂, SO₂, NO₂, and CO were commercially purchased from air gas material with a purity of 99.999% of known concentration and used to achieve different gaseous environments in the chamber. Further, various concentrations of H₂S were achieved by mixing synthetic air and H₂S gas in the mixing chamber with pre-defined gas flow rates controlled by mass flow controllers. The desired relative humidity (RH) was achieved in the sensing chamber by blowing synthetic air through a saturated aqueous solution of different salts viz. NaCl, KCl, and K₂SO₄ to generate approximately 75%, 86%, and 97.5% relative humidity, respectively. To validate the repeatability of the sensor response, the fabricated device for exposed to H₂S gas for 25 consecutive cycles. The sensitivity of gas was used to determine the limit of detection (LOD) and limit of quantification (LOQ). The LOD is expressed as the lowest concentration of H₂S that can be detected by the sensor while LOQ is defined as the lowest amount of H₂S that can be quantitatively detected with precision and accuracy [35]. The LOD and LOQ of the gas sensor are calculated from:
$$LOD = \frac{3 \times \text{standard deviation}}{\text{slope}}$$
(2.2)

$$LOQ = \frac{10 \times \text{standard deviation}}{\text{slope}}$$
(2.3)

where the standard deviation is the deviation of response in air and slope is the slope of the linear part of the calibrated curve [34,36].



2.4 Results and Discussion

Figure 2.1 (a) Schematic representation of COPO synthesis *via* mechanochemical method and gas sensing device fabrication on IDEs. (b) PXRD patterns of 1,3,5-benzenetricarbonyl trichloride, 3,4-diaminobenzhydrazide, COPO and COPS, and (c) FT-IR spectra of 1,3,5-benzenetricarbonyl trichloride, 3,4-diaminobenzhydrazide, COPO and COPS.

The powder X-ray diffraction (PXRD) pattern was used to determine the nature of the monomers and as-synthesized COPs. The PXRD patterns of 1,3,5-benzenetricarbonyl trichloride and 3,4-diaminobenzhydrazide show sharp peaks, indicating that the monomers are crystalline. However, the PXRD patterns of COPO and COPS show a broad peak, indicating that both polymers are amorphous (**Figure 2.1b**) [29]. The successful formation of amide and thioamide bonds in COPO and COPS was

characterized by Fourier transform infrared (FT-IR) analysis. Figure **2.1c** displays the FT-IR spectra of 1,3,5-benzenetricarbonyl trichloride, 3,4-diaminobenzhydrazide, COPO and COPS. The FT-IR spectrum of 1,3,5-benzenetricarbonyl trichloride exhibits a peak at 1751 cm⁻¹, which is attributed to the stretching frequency of C=O, and a peak at 701 cm⁻¹, which is ascribed to the stretching frequency of C-Cl. In the spectrum of 3.4-diaminobenzhydrazide, a stretching frequency of 3320 cm^{-1} is observed, corresponding to the NH group. The FT-IR spectrum of COPO shows significant peaks at 1646 and 1511 cm⁻¹, which correspond to the stretching frequency of the amide I (C=O) and amide II (NH) bands, respectively [37,27]. The significant shift in the peak of C=O and the disappearance of the peak of acid chloride of 1,3,5-benzenetricarbonyl trichloride in the FT-IR spectrum of COPO confirm the formation of amide bonds in the COPO. In addition, the FT-IR spectrum of COPS shows notable peaks at 1488, 1321, 1026, and 726 cm⁻¹, which correspond to the vibrational stretching frequencies of NH, C-N, C=S, and NCS bands, respectively [38,39]. A slight change in the bending frequency of N-H and the appearance of a peak at 1026 cm⁻¹ (corresponding to C=S) confirm the presence of C=S bond in the COPS.



Figure 2.2 ¹³C CP-MAS solid-state NMR of (a) COPO and (b) COPS. Nitrogen (N₂) adsorption/desorption isotherm of (c) COPO and (d) COPS (inset figures pore diameter curve of COPO and COPS, respectively, calculated by BJH method).

Moreover, the formation of the amide and thioamide bonds in the COPO and COPS was also confirmed by the solid-state cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance (¹³C CP-MAS NMR spectrum) (**Figure 2.2**). The ¹³C CP-MAS NMR spectrum of the COPO indicates two types of carbon at chemical shifts of 129.9 and 166 ppm, which correspond to the carbon in the aromatic ring (C=C) and amide bond (C=O), respectively (**Figure 2.2a**) [37]. On the other hand, the ¹³C CP-MAS NMR spectrum of the COPS reveals two types of carbon at chemical shifts of 128.8 and 174 ppm corresponding to the carbon in the aromatic ring (C=S), respectively (**Figure 2.2b**) [40]. The ¹³C CP-MAS NMR spectra provide confirmation of the successful formation of COPO and COPS.



Figure 2.3 (a) Thermal stability graph of the COPO and COPS and (b) DSC curves of COPO and COPS on the second heating scan.

Furthermore, the Brunauer–Emmett–Teller (BET) surface area and porosity of COPO and COPS were determined using nitrogen sorption analysis at 77 K. Both COPO and COPS exhibit type IV sorption isotherm curves (**Figure 2.2c and 2.2d**) [41,42]. The calculated BET surface area (S_{BET}) of COPO was found to be 21.6 m²/g, while for COPS it was 10.2 m²/g. COPO exhibits a larger S_{BET} compared to COPS. In addition, pore size distribution of COPO and COPS was determined using the BJH method and the values were found to be 3.5 nm and 3.4 nm, respectively (**inset Figure 2.2c and 2.2d**). To study the thermal stability behavior of COPO and COPS, a thermogravimetric (TGA) experiment was performed under a dry nitrogen atmosphere within a

Chapter 2

temperature range of 27 to 800 °C (**Figure 2.3a**). Initially, a small weight loss is observed up to 260 °C for both COPO and COPS, which can be attributed to residual solvents and moisture trapped in the samples [43]. The major and gradual weight loss was observed within 260 to 570 °C and within 260 to 700 °C for COPO and COPS. This weight loss is attributed to the disintegration of functional groups in both COPO and COPS [44]. The results of the TGA curves indicate that both COPO and COPS have promising thermal stability. To gain further insight into their thermal properties, a differential scanning calorimetry (DSC) experiment was performed (**Figure 2.3b**). However, no significant peak indicating a glass-transition temperature was observed in the DSC curves.



Figure 2.4 FE-SEM image of (a) COPO and (b) COPS. (c)-(f) EDS pattern and elemental mapping of COPO. (g)-(j) EDS pattern and elemental mapping of COPS.

The surface morphologies of COPO and COPS were observed using field emission scanning electron microscopy (FE-SEM), high-resolution transmission electron microscopy (HR-TEM), and atomic force microscopy (AFM) images. COPO shows an irregular buffy stack morphology (**Figure 2.4a**), while COPS indicates a rough morphology

(Figure 2.4b) [45] However, a higher magnification FE-SEM image of COPS reveals cauliflower-like morphology (inset Figure 2.4b) [46]. Additionally, the energy-dispersive X-ray spectroscopy (EDS) spectrum and elemental mapping of COPO confirm the presence and uniform distribution of C, N, and O on the surface (Figure 2.4c-2.4f). Similarly, the EDS spectrum and elemental mapping of COPS confirm the presence and uniform distribution of C, N, and S over the surface (Figure 2.4g-2.4j).



Figure 2.5 High-resolution TEM images of (a) COPO (inset SAED pattern) and (b) COPS (inset SAED pattern). AFM images of (c) COPO and (d) COPS.

Further, the HR-TEM technique was used to confirm the FE-SEM images of COPO and COPS. It was observed that the HR-TEM images of COPO and COPS align with the FE-SEM results (**Figure 2.5a and 2.5b**) [44]. Additionally, the selected area electron diffraction (SAED) patterns of COPO and COPS exhibited an amorphous structure (**inset Figure 2.5a and 2.5b**) [47]. To further validate the FE-SEM findings, AFM analysis was also conducted on COPO and COPS. The 2D AFM images of COPO and COPS confirm the presence of irregular buffy stack

morphology and cauliflower-like morphology, respectively (Figure 2.5c and 2.5d).

2.4.1 H₂S Sensing Performance of the COPO and COPS

The gas sensing performances of the COPO and COPS sensors were investigated by measuring the change in electrical resistance when exposed to H₂S under ambient conditions (25 °C, 45% relative humidity (RH)). Before exposing the H₂S molecules, the COPO and COPS sensors were kept inside the sensing chamber for a while in ambient conditions to obtain a stable base resistance. Afterwards, the sensors were exposed to H₂S, a reducing gas, which results in an increase in resistance. This increase in resistance demonstrates that both COPO and COPS sensors have a the p-type nature [48]. The response value of the COPO sensor to 100 ppm H₂S is found to be 190%, while that of the COPS sensor is found to be 73% (**Figure 2.7a**). The response and recovery times for the COPO and COPS sensors are found to be 20/40 s and 30/50 s (**Figure 2.7b and 2.6a**), respectively.



Figure 2.6 (a) Single transient response-recovery cycle of the COPS sensor to 100 ppm H₂S at 25 °C. Transient resistance response of the (b) COPO and (c) COPS sensors to 100 ppm H₂S at 25 °C.

Additionally, the transient resistance response of the COPO and COPS sensors to H_2S at 25 °C is displayed in **Figure 2.6b and 2.6c.** The COPO sensor is restores to its base resistance, while the COPS sensor does not fully recover to its 90% base resistance value. **Figure 2.7b** illustrates the transient graph, which depicts the response and recovery time of the COPO sensor for a single cycle of H_2S exposure at 25 °C. It is evident from **Figure 2.7a** that the COPO sensor exhibits a higher response with a shorter response/recovery time and complete recovery compared to the

COPS sensor, revealing a faster adsorption and desorption process of H_2S molecules from the surface of the COPO sensor. Therefore, further sensing experiments were conducted by using the COPO sensor.



Figure 2.7 (a) The response of COPO and COPS fabricated sensor towards 100 ppm H_2S . (b) Single transient response-recovery cycle of the COPO towards 100 ppm H_2S . (c) Selectivity of the COPO sensor against other gases at different concentrations. (d) Dynamic response of COPO sensor for H_2S from 100 ppm to 100 ppb. (e) The linear fitting curve of response and concentration of H_2S and (f) effect of RH on sensing performance of COPO towards 100 ppm H_2S .

Further, the selectivity of COPO-based sensors has been studied for various oxidizing and reducing gases at different concentrations (**Figure 2.7c**). The COPO sensor exhibits a response of 190%, 70%, 104%, 69%, and 95% to H_2S (100 ppm), NO₂ (100 ppm), SO₂ (100 ppm), CO₂ (500

ppm), and CO (200 ppm), respectively. Therefore, COPO shows adequate selectivity towards H_2S in comparison to other interfering gases.

We investigated the dynamic transient profile of the COPO sensor under different concentrations of H_2S , ranging from 100 to 0.1 ppm (**Figure 2.7d**). The results demonstrate that as the concentration of H_2S decreases from 100 to 0.1 ppm, the response of the COPO sensor also decreases from 190% to 71%, respectively. **Figure 2.7d** depicts that even at parts per billion exposure of H_2S gas, the COPO sensor exhibits a significant response, which is the OSHA short-term exposure limit. **Figure 2.7e** determines the correlation between H_2S concentration and response, indicating that the COPO sensor has a limit of detection (LOD) value of 0.75 ppb and a limit of quantification (LOQ) value of 2.5 ppb.



Figure 2.8 (a) Response of the COPO sensor to 100 ppm H_2S for 25 consecutive cycles at 25 °C and (b) response of the COPO sensor to 100 ppm H_2S for 2 months at 25 °C.

The response of COPO towards H_2S was investigated under different relative humidity (RH) levels, as it is a major factor for practical gas sensing applications (**Figure 2.7f**). The response of COPO towards H_2S at 75, 86, and 97.5% RH was found to be 69, 60, and 49%, respectively. Based on these results, it can be concluded that as the RH increases in the sensing chamber, the response towards H_2S decreases. This is because as the RH increases, more H_2O molecules are adsorbed on the surface of COPO, limiting the number of active sites accessible for H_2S molecule adsorption [49]. Therefore, as the relative humidity increases, it becomes difficult for H_2S molecules to adsorb on the surface. It is observed that the COPO based sensor does not fully recover when the RH is increased at 25 °C, because the H_2S and water molecules do not completely desorb. However, even though the response at higher humidity levels compared to atmospheric humidity, the COPO sensor still exhibits a significant response (49%) even at 97.5% RH.

Moreover, we conducted a study to assess the repeatability of the COPO sensor. We exposed the COPO sensor to 100 ppm of H₂S for 25 consecutive cycles in the sensing chamber at 25 °C. The results, as shown in **Figure 2.8a**, indicate that there is no noticeable change in the COPO sensor's response after repeated exposure to H₂S. This suggests that the COPO sensor shows good repeatability and fully recovers after each exposure to H₂S. Consequently, we examined the long-term stability of the COPO sensor by exposing it to 100 ppm H₂S at 25 °C every 5th day for a period of 2 months (**Figure 2.8b**). The COPO sensor shows slight changes in its response, which could be attributed to the change in environmental conditions. Therefore, the COPO sensor may provide a fresh perspective for the design of advanced sensing devices.

Table 2.1 shows a comparative study of an H_2S sensing experiment using the COPO sensor and previously reported sensors. It has been observed from **Table 2.1** that the COPO sensor reported in this paper exhibits an excellent response of 190% towards H_2S under ambient conditions, compared to other reports. This makes it a promising device for monitoring environmental pollution and human health.

S.	Material	Conce	Resp	Tempe	Respo	LOD	Refe
No.		ntratio	onse	rature	nse/re		renc
		n		(°C)	cover		es
		(ppm)			y time		
1.	Cu-doped	100	0.87	24	14/32	136	[50]
	ZnO/RGO		%		S	ppb	
2.	MOF-	50	97%	25	< 8/30	NA	[51]
	5/CS/IL				S		
	membrane						

Table 2.1 Comparative study of various H₂S gas sensors with COPO

Chapter 2

۶.		100	%			nnh	work
9.	СОРО	100	190	25	20/40	0.75	This
8.	СОР	200	50%	25	9/12 s	NA	[57]
	SICI				2h		
	sker	-		-	4min/		E 1
7.	In ₂ O ₃ whi	10	37%	25	1-	NA	[56]
	/SnO ₂				S		
6.	PANI/rGO	100	56%	25	35/40	NA	[55]
	TiO ₂ -20		1%		S	ppm	
5.	p-CuO/n-	100	46.8	25	41/92	3	[54]
	ne oxide						
	polyethyle						
	—				50 s		
4.	polyaniline	10	25%	25	120/2	NA	[53]
	ZnO		8%		S		
3.	CuO doped	1	83.9	200	9/160	NA	[52]

(*NA = not available)

2.4.2 H₂S Mechanism

The mechanism of H₂S gas sensing through H-bonding has been previously outlined [8]. The detection of H₂S gas relies on changes in resistance in a sensor made of polymer. These changes occur mainly due to the mobility of protons through amide or thioamide bonds. The COPO and COPS polymers have amide and thioamide functional groups, respectively, which provide a pathway for NH protons to move through enol forms of both polymers (Scheme 2.2). The presence of abundant amide and thioamide bonds in the COPO and COPS polymers increases their basicity, indirectly enhancing their sensitivity and selectivity towards acidic gases like H₂S. Upon the exposure of H₂S gas to the surface of COPO and COPS sensors, the conduction of protons decreases. This is because of the interaction between H₂S and the polymer, specifically the H-N-(C=O) and H-N-(C=S) groups. The formation of the enol is also inhibited, which further decreases the transportation of protons on the surface of the polymers. H₂S molecules interact with the HN-C=O (COPO) and HN-C=S (COPS) groups through H-bonding, which strongly inhibits the conduction of protons on the polymer surface. As a result, the resistance of the COPO and COPS increases, indicating that they have a p-type nature [48,58].

Scheme 2.2 Interaction of amide and thioamide bonds in the COPO and COPS with H_2S molecules

The COPO sensor exhibited better sensing performance compared to COPS sensor when exposed to H₂S molecules on the surface. This could be because COPO has a larger BET surface area ($S_{BET} = 21.6 \text{ m}^2/\text{g}$), which offers more active sites for the interaction between H₂S molecules and NH of COPO [59]. On the other hand, COPS has fewer active sites available for interaction with H₂S molecules due to its smaller BET surface area (S_{BET} = $10.2 \text{ m}^2/\text{g}$). Therefore, more H₂S molecules would interact with NH through H-bonding in COPO compared to COPS, leading to a significant change in resistance observed in the COPO sensor. Consequently, the sensing response to H₂S gas molecules is found to be higher in COPO (response = 190%) compared to COPS (response = 73%). Moreover, the presence of a large number of active sites on the surface of the COPO sensor increases the adsorption and desorption process of H₂S molecules, resulting in complete recoverability [59,49]. Therefore, COPO exhibits a higher response to H₂S with complete recovery.

Furthermore, it has been observed that when the concentration of H_2S gas increases, the resistance of the COPO sensor also increases rapidly. This could be due to the interaction of more H_2S molecules with the amide bonds of COPO, which drastically inhibits the conduction of protons on the surface. As a result, the response of the COP sensor to H_2S increases. The response of the COPO sensor to H_2S gas was also examined at higher temperature. The base resistance of the COPO is not stable at higher temperatures, which could be due to higher molecular vibrations in the bonds of the COP. Therefore, at higher temperature, H_2S molecules do not interact accurately with amide bonds and inhibit the interaction of COPO with H_2S gas. One interesting fact in this report

is that the resistance of the COPO sensor decreases in the presence of relative humidity (RH), which could be attributed to proton conduction. The possible reason for this is that as RH% increases (more H_2O molecules), there are protons available for conduction. As a result, water molecules provide an alternative route for proton conduction on the surface of COPO [60,61,62,63]. Therefore, the resistance of COPO decreases as RH increases; as a result, the trade-off between H_2S and H_2O decreases the response of COPO to H_2S .

2.5 Conclusion

In summary, we have successfully reported on the role of amide- and thioamide-decorated covalent organic polymers for selective chemodetection of H₂S at room temperature. We characterized the COPO and COPS using various techniques such as PXRD, FT-IR, ¹³C CP-MAS NMR, BET, TGA, FE-SEM, TEM, and AFM. Furthermore, we tested both COPO and COPS for gas sensing at 25 °C. Among them, the COPO sensor demonstrated a good sensing performance of 190% with a fast response/recovery time of 20/40 s to 100 ppm H₂S at 25 °C. The presence of abundant polar amide bonds in COPO facilitated the selective detection of H₂S through a proton conduction mechanism. In addition, the LOD and LOQ for COPO were found to be 0.75 ppb and 2.5 ppb, respectively. The COPO and COPS sensors showed adequate selectivity for detecting H₂S in the presence of other interfering reducing and oxidizing gases. Moreover, the COPO showed good repeatability, complete reversibility, and long-term stability. These results indicate that COPO is an exceptional material for selectively detecting H₂S and suggest its potential use as an H₂S sensor for environmental monitoring.

2.6 References

 Liu L., Wang Y., Dai Y., Li G., Wang S., Li T., Zhang T., Qin S.
 (2019), In Situ Growth of NiO@SnO₂ Hierarchical Nanostructures for High-Performance H₂S Sensing, ACS Appl. Mater. Interfaces, 11, 44829–44836 (DOI: 10.1021/acsami.9b13001). (2) Wu Z., Li Z., Li H., Sun M., Han S., Cai C., Shen W., Fu Y. (2019), Ultrafast Response/Recovery and High Selectivity of H₂S Gas Sensor Based on α -Fe₂O₃ Nano-Ellipsoids from One-Step Hydrothermal Synthesis, ACS Appl. Mater. Interfaces, 11, 12761–12769 (DOI: 10.1021/acsami.8b22517).

(3) Lee M. H., Vikrant K., Younis S. A., Szulejko J. E., Kim K. H.
(2020), Chemisorption of Hydrogen Sulfide by Metal-Organic
Frameworks and Covalent-Organic Polymers Based on
Experimental/Theoretical Evaluation, J. Clean. Prod., 250, 119486 (DOI: 10.1016/j.jclepro.2019.119486).

(4) Shaik R., Kampara R. K., Kumar A., Sharma C. S., Kumar M.
(2022), Metal Oxide Nanofibers Based Chemiresistive H₂S Gas Sensors, Coord. Chem. Rev., 471, 214752, (DOI: 10.1016/j.ccr.2022.214752).

Patel C., Mandal B., Jadhav R. G., Ghosh T., Dubey M., Das A.
K., Htay M. T., Atuchin V. V., Mukherjee S. (2022), S, N Co-Doped
Carbon Dot-Functionalized WO3 Nanostructures for NO₂ and H₂S
Detection, ACS Appl. Nano Mater., 5, 2492-2500, (DOI: 10.1021/acsanm.1c04174).

Wu J., Yue G., Chen W., Xing Z., Wang J., Wong W. R., Cheng Z., Set S. Y., Murugan G. S., Wang X., Liu T. (2020), On-Chip Optical Gas Sensors Based on Group-IV Materials, ACS Photonics, 7, 2923–2940 (DOI: 10.1021/acsphotonics.0c00976).

(7) He M., Croy R. G., Essigmann J. M., Swager T. M. (2019),
Chemiresistive Carbon Nanotube Sensors for N-Nitrosodialkylamines,
ACS Sensors, 4, 2819–2824, (DOI: 10.1021/acssensors.9b01532).

(8) Maiti S., Mandal B., Sharma M., Mukherjee S., Das A. K. (2020), A Covalent Organic Polymer as an Efficient Chemosensor for Highly Selective H_2S Detection through Proton Conduction, Chem. Commun., 56, 9348–9351 (DOI: 10.1039/D0CC02704A).

(9) Kaushik A., Kumar R., Arya S. K., Nair M., Malhotra B. D., Bhansali S. (2015), Organic-Inorganic Hybrid Nanocomposite-Based Gas Sensors for Environmental Monitoring, Chem. Rev., 115, 4571– 4606 (DOI: 10.1021/cr400659h). (10) Liu X., Zheng W., Kumar R., Kumar M., Zhang J. (2022),
Conducting Polymer-Based Nanostructures for Gas Sensors, Coord.
Chem. Rev., 462, 214517 (DOI: 10.1016/j.ccr.2022.214517).

(11) Park K. R., Cho H. B., Lee J., Song Y., Kim W. B., Choa Y. H.
(2020), Design of Highly Porous SnO₂-CuO Nanotubes for Enhancing H₂S Gas Sensor Performance, Sensors Actuators, B Chem., 302, 127179
(DOI: 10.1016/j.snb.2019.127179).

(12) Pradhan A., Manna R. N. (2021), Surface-Modified Covalent Organic Polymer for Metal-Free Electrocatalytic Hydrogen Evolution Reaction, ACS Appl. Polym. Mater., 3, 1376–1384 (DOI: 10.1021/acsapm.0c1238).

(13) Cui W. R., Zhang C. R., Jiang W., Liang R. P., Wen S. H., Peng D., Qiu J. D. (2019), Covalent Organic Framework Nanosheet-Based Ultrasensitive and Selective Colorimetric Sensor for Trace Hg²⁺ Detection, ACS Sustain. Chem. Eng., 7, 9408–9415 (DOI: 10.1021/acssuschemeng.9b00613).

(14) Nouruzi N., Dinari M., Gholipour B., Afshari M., Rostamnia S. (2022), In Situ Organized Pd and Au Nanoparticles in a Naphthalene-Based Imine-Linked Covalent Triazine Framework for Catalytic Suzuki Reactions and H₂ Generation from Formic Acid, ACS Appl. Nano Mater, 5, 6241–6248 (DOI: 10.1021/acsanm.2c00285).

(15) Dey K., Mohata S., Banerjee R. (2021), Covalent Organic
Frameworks and Supramolecular Nano-Synthesis, ACS Nano, 15, 12723–12740 (DOI: 10.1021/acsnano.1c05194).

(16) Cui W. R., Zhang C. R., Jiang W., Li F. F., Liang R. P., Liu J.,
Qiu J. D. (2020), Regenerable and Stable sp² Carbon-Conjugated
Covalent Organic Frameworks for Selective Detection and Extraction of
Uranium, Nat. Commun., 11, 436 (DOI: 10.1038/s41467-020-14289-x).

(17) El-Mahdy A. F. M., Young C., Kim J., You J., Yamauchi Y., Kuo S. W. (2019), Hollow Microspherical and Microtubular [3+3] Carbazole-Based Covalent Organic Frameworks and Their Gas and Energy Storage Applications, ACS Appl. Mater. Interfaces, 11, 9343– 9354 (DOI: 10.1021/acsami.8b21867). (18) Bhadra M., Kandambeth S., Sahoo M. K., Addicoat M., Balaraman E., Banerjee R. (2019), Triazine Functionalized Porous Covalent Organic Framework for Photo-Organocatalytic E-Z Isomerization of Olefins, J. Am. Chem. Soc., 141, 6152–6156 (DOI: 10.1021/jacs.9b01891).

(19) Patra B. C., Khilari S., Manna R. N., Mondal S., Pradhan D., Pradhan A., Bhaumik A. (2017), A Metal-Free Covalent Organic Polymer for Electrocatalytic Hydrogen Evolution, ACS Catal., 7, 6120– 6127 (DOI: 10.1021/acscatal.7b01067).

(20) Yadav D., Awasthi S. K. (2021), Ni Nanoparticle-Immobilized Imine-Linked Microspherical Covalent Organic Polymer for Degradation Studies of Organic Dyes, ACS Appl. Polym. Mater., 3, 5460–5469 (DOI: 10.1021/acsapm.1c00793).

(21) Meng Z., Stolz R. M. Mirica K. A. (2019), Two-Dimensional Chemiresistive Covalent Organic Framework with High Intrinsic Conductivity, J. Am. Chem. Soc., 141, 11929–11937 (DOI: 10.1021/jacs.9b03441).

(22) Barreda O., Taggart G. A., Rowland C. A., Yap G. P. A., Bloch
E. D. (2018), Mechanochemical Synthesis of Porous Molecular
Assemblies, Chem. Mater, 30, 3975–3978 (DOI: 10.1021/acs.chemmater.8b01667).

(23) Szczesniak B., Borysiuk S., Choma J., Jaroniec M. (2020)
Mechanochemical Synthesis of Highly Porous Materials, Mater.
Horizons, 7, 1457–1473 (DOI: 10.1039/D0MH0081G).

(24) Friščić T., Mottillo C., Titi H. M. (2020), Mechanochemistry for Synthesis, Angew. Chemie, 132, 1030–1041 (DOI: 10.1002/anie.201906755).

(25) Chen Y., Li W., Wang X., Gao R., Tang A. N., Kong D. M.
(2021), Green Synthesis of Covalent Organic Frameworks Based on Reaction Media, Mater. Chem. Front., 5, 1253–1267 (DOI: 10.1039/D0QM00801J).

(26) Boldyreva E. (2013), Mechanochemistry of Inorganic and Organic Systems: What Is Similar, What Is Different?, Chem. Soc. Rev., 42, 7719–7738 (DOI: 10.1039/C3CS60052A).

(27) Rajput L., Banerjee R. (2014), Mechanochemical Synthesis of Amide Functionalized Porous Organic Polymers, Cryst. Growth Des., 14, 2729–2732 (DOI: 10.1021/cg.500439f).

(28) Zulfiqar S., Sarwar M. I., Yavuz C. T. (2014), Melamine Based
Porous Organic Amide Polymers for CO₂ Capture, RSC Adv., 4, 52263–
52269, (DOI: 10.1039/C4RA11442F).

(29) Suresh V. M., Bonakala S., Atreya H. S., Balasubramanian S., Maji T. K. (2014), Amide Functionalized Microporous Organic Polymer (Am-MOP) for Selective CO₂ Sorption and Catalysis, ACS Appl. Mater. Interfaces, 6, 4630–4637 (DOI: 10.1021/am500057z).

(30) Lee H. J., Choi Y. S., Lee K. B., Park J., Yoon C. J. (2002), Hydrogen Bonding Abilities of Thioamide, J. Phys. Chem. A, 106, 7010–7017, (DOI: 10.1021/jp025516e).

(31) Camacho L. A., Lampkin B. J., Vanveller B. (2019), A Bottomup Approach to Preserve Thioamide Residue Stereochemistry during FMOC Solid-Phase Peptide Synthesis, Org. Lett., 21, 7015–7018, DOI: 10.1021/acs.orglett.9b02598.

(32) Verma H., Khatri B., Chakraborti S., Chatterjee J. (2018), Increasing the Bioactive Space of Peptide Macrocycles by Thioamide Substitution, Chem. Sci., 9, 2443–2451, (DOI: 10.1039/C7SC04671E).

(33) Patel C., Mandal B., Jadhav R. G., Ghosh T., Dubey M., Das A.
K., Htay M. T., Atuchin V. V., Mukherjee S. (2021), S, N Co-Doped Carbon Dot-Functionalized WO₃ Nanostructures for NO₂ and H₂S Detection, ACS Appl. Nano Mater., 5, 2492–2500 (DOI: 10.1021/acsanm.1c04174).

(34) Yang K., Yuan W., Hua Z., Tang Y., Yin F., Xia D. (2020), Triazine-Based Two-Dimensional Organic Polymer for Selective NO₂ Sensing with Excellent Performance, ACS Appl. Mater. Interfaces, 12, 3919–3927 (DOI: 10.1021/acsami.9b17450).

(35) Jha R. K., D'Costa J. V., Sakhuja N., Bhat N. (2019), MoSe₂ Nanoflakes Based Chemiresistive Sensors for Ppb-Level Hydrogen Sulfide Gas Detection, Sensors Actuators, B Chem., 297, 126687 (DOI: 10.1016/j.snb.2019.126687). (36) Rathi K., Pal K. (2020), Wireless Hand-Held Device Based on Polylactic Acid-Protected, Highly Stable, CTAB-Functionalized Phosphorene for CO₂ Gas Sensing, ACS Appl. Mater. Interfaces, 12, 38365–38375 (DOI: 10.1021/acsami.0c10285).

(37) Liu Z., Ou J., Wang H., You X., Ye M. (2016), Synthesis and Characterization of Hydrazide-Linked and Amide-Linked Organic Polymers, ACS Appl. Mater. Interfaces, 8, 32060–32067, (DOI: 10.1021/acsami.6b11572).

(38) Kulkarni C., Berrocal J. A., Lutz M., Palmans A. R. A., Meijer E.
W. (2019), Directing the Solid-State Organization of Racemates via Structural Mutation and Solution-State Assembly Processes, J. Am. Chem. Soc., 141, 6302–6309 (DOI: 10.1021/jacs.9b00452).

(39) Coban Z. G., Yagci Y., Kiskan B. (2021), Catalyzing the Ring-Opening Polymerization of 1,3-Benzoxazines via Thioamide from Renewable Sources, ACS Appl. Polym. Mater., 3, 4203–4212 (DOI: 10.1021/acsapm.1c00637).

(40) Jena S., Routray C., Dutta J., Biswal H. S. (2022), Hydrogen Bonding Directed Reversal of ¹³C NMR Chemical Shielding, Angew. Chemie - Int. Ed., 61, e202207 (DOI: 10.1002/anie.202207521). https://doi.org/10.1002/anie.202207521.

(41) Roy Chowdhury A., Maiti S., Mondal A., Das A. K. (2020), Picolinohydrazide-Based Covalent Organic Polymer for Metal-Free Catalysis and Removal of Heavy Metals from Wastewater, J. Phys. Chem. C, 124, 7835–7843 (DOI: 10.1021/acs.jpcc.0c00664).

(42) Rezaei F., Dinari M. (2021) Novel Covalent Organic Polymer-Supported Ag Nanoparticles as a Catalyst for Nitroaromatics Reduction, Colloids Surfaces A Physicochem. Eng. Asp., 618, 126441 (DOI: 10.1016/j.colsurfa.2021.126441).

(43) Yadav D., Awasthi S. K. (2020), A Pd Confined Hierarchically Conjugated Covalent Organic Polymer for Hydrogenation of Nitroaromatics: Catalysis, Kinetics, Thermodynamics and Mechanism, Green Chem., 22, 4295–4303 (DOI: 10.1039/D0GC01469A). (44) Yadav D., Awasthi S. K. (2019), An Unsymmetrical Covalent Organic Polymer for Catalytic Amide Synthesis, Dalt. Trans., 49, 179– 186 (DOI: 10.1039/C9DT03931G).

(45) Ramasamy R. P., Yang K., Rafailovich M. H. (2014), Polypropylene-Graphene-a Nanocomposite That Can Be Converted into a Meta-Material at Desired Frequencies, RSC Adv., 4, 44888–44895 (DOI: 10.1039/C4RA05814C).

(46) Sahoo B. N., Balasubramanian K. (2014), Facile Synthesis of Nano Cauliflower and Nano Broccoli like Hierarchical Superhydrophobic Composite Coating Using PVDF/Carbon Soot Particles via Gelation Technique, J. Colloid Interface Sci., 436, 111–121 (DOI: 10.1016/j.jcis.2014.08.031).

(47) Zhang P., Han B., Yang X., Zou Y., Lu X., Liu X., Zhu Y., Wu D., Shen S., Li L., Zhao Y., Francisco J. S., Gu M. (2022), Revealing the Intrinsic Atomic Structure and Chemistry of Amorphous LiO₂-Containing Products in Li-O₂ Batteries Using Cryogenic Electron Microscopy, J. Am. Chem. Soc., 144, 2129–2136 (DOI: 10.1021/jacs.1c10146).

(48) Kanaparthi S., Singh S. G. (2019), Solvent-Free Fabrication of a Room Temperature Ammonia Gas Sensor by Frictional Deposition of a Conducting Polymer on Paper, Org. Electron., 68, 108–112 (DOI: 10.1016/j.orgel.2019.01.053).

(49) Gasso S., Sohal M. K., Mahajan A. (2022), MXene Modulated SnO₂ Gas Sensor for Ultra-Responsive Room-Temperature Detection of NO₂, Sensors Actuators B Chem., 357, 131427 (DOI: 10.1016/j.snb.2022.131427).

(50) Shewale P. S., Yun K. S. (2020), Synthesis and Characterization of Cu-Doped ZnO/RGO Nanocomposites for Room-Temperature H₂S Gas Sensor, J. Alloys Compd., 837, 155527 (DOI: 10.1016/j.jallcom.2020.155527).

(51) Ali A., Alzamly A., Greish Y. E., Bakiro M., Nguyen H. L., Mahmoud S. T. (2021), A Highly Sensitive and Flexible Metal-Organic Framework Polymer-Based H₂S Gas Sensor, ACS Omega, 6 (27), 17690–17697. https://doi.org/10.1021/acsomega.1c02295. (52) Hsu K. C., Fang T. H., Hsiao Y. J., Li Z. J. (2021), Rapid Detection of Low Concentrations of H₂S Using CuO-Doped ZnO Nanofibers, J. Alloys Compd., 852, 157014 (DOI: 10.1016/j.jallcom.2020.157014).

(53) Mousavi S., Kang K., Park J., Park I. (2016), A Room Temperature Hydrogen Sulfide Gas Sensor Based on Electrospun Polyaniline-Polyethylene Oxide Nanofibers Directly Written on Flexible Substrates, RSC Adv., 6, 104131–104138 (DOI: 10.1039/c6ra20710c).

(54) He H., Zhao C., Xu J., Qu K., Jiang Z., Gao Z., Song Y. Y. (2021), Exploiting Free-Standing p-CuO/n-TiO₂ Nanochannels as a Flexible Gas Sensor with High Sensitivity for H_2S at Room Temperature, ACS Sensors, 6, 3387–3397 (DOI: 10.1021/acssensors.1c01256).

(55) Saravanan K. K., Siva Karthik P., Mirtha P. R., Balaji J., Rajeshkanna B. (2020), A One-Pot Hydrothermal-Induced PANI/SnO₂ and PANI/SnO₂/RGO Ternary Composites for High-Performance Chemiresistive-Based H₂S and NH₃ Gas Sensors, J. Mater. Sci. Mater. Electron., 31, 8825–8836 (DOI: 10.1007/s10854-020-03417-4).

(56) Kaur M., Jain N., Sharma K., Bhattacharya S., Roy M., Tyagi A.
K., Gupta S. K., Yakhmi J. V. (2008), Room-Temperature H₂S Gas
Sensing at Ppb Level by Single Crystal In₂O₃ Whiskers, Sensors
Actuators, B Chem., 133, 456–461 (DOI: 10.1016/j.snb.2008.03.003).

(57) Xu H., Li J., Fu Y., Li P., Luo W., Tian Y. (2020), A Covalent Organic Polymer as an Efficient Chemosensor for Highly Selective H₂S Detection through Proton Conduction. *ACS Appl. Nano Mater.*, 3, 8075– 8087 (DOI: 10.1021/acsanm.0c01533).

Mandal B., Maiti S., Aaryashree, Siddharth G., Das M., Agarwal A., Das A. K., Mukherjee S. (2020), Organo-Di-Benzoic-Acidified ZnO Nanohybrids for Highly Selective Detection of CO at Low Temperature, J. Phys. Chem., 124, 7307–7316 (DOI: 10.1021/acs.jpcc.0c01044).

(59) Duan X., Duan Z., Zhang Y., Liu B., Li X., Zhao Q., Yuan Z., Jiang Y., Tai H. (2022), Enhanced NH₃ Sensing Performance of Polyaniline via a Facile Morphology Modification Strategy, Sensors Actuators B Chem., 369, 132302 (DOI:10.1016/j.snb.2022.132302). (60) Amit M., Yuran S., Gazit, E., Reches M., Ashkenasy N. (2018),
Tailor-Made Functional Peptide Self-Assembling Nanostructures, Adv.
Mater., 30, 1707083 (DOI: 10.1002/adma.201707083).

(61) Lerner Yardeni J., Amit M., Ashkenasy G., Ashkenasy N. (2016),
Sequence Dependent Proton Conduction in Self-Assembled Peptide
Nanostructures, Nanoscale, 8, 2358–2366 (DOI: 10.1039/C5NR06750B).

(62) Sung T., Namgung S. D., Lee J., Choe I. R., Nam K. T., Kwon J.
Y. (2018), Effects of Proton Conduction on Dielectric Properties of Peptides, RSC Adv., 8, 34047–34055 (DOI: 10.1039/C8RA06121A).

(63) Ma C., Dong J., Viviani M., Tulini I., Pontillo N., Maity S., Zhou
Y., Roos W. H., Liu K., Herrmann A., Portale G. (2020), De Novo
Rational Design of a Freestanding, Supercharged Polypeptide, ProtonConducting Membrane, Sci. Adv., 6, eabc0810 (DOI: 10.1126/sciadv.abc0810).

Chapter 3

Tailoring Thiazole Decorated Polymer withBenzoselenadiazoleforEnhancedSO2Sensing

Chapter 3

3.1 Introduction

Conjugated polymers (CPs) are a subset of polymers with a π -conjugated system. CPs have garnered enormous attention due to their wide application in sensors, supercapacitors, energy storage, photovoltaics, organic field-effect transistors (OFET), and optoelectronics [1,2,3,4,5]. The interaction between the chains of the CPs decreases the HOMO-LUMO gap, resulting in improved electrical properties [6,7]. Moreover, the introduction of heteroatoms in the conjugated polymers can enhance the performances of the derived devices. Recently, CPs have been considered as a preferable option to inorganic semiconductors for sensing materials used in detecting toxic gases. This is because they possess unique properties such as excellent sensitivity, selectivity, improved electrical properties, light weight, ability to operate at room temperature, and flexibility. These properties are achieved by introducing specific functional groups into the side chain of the CPs [3,8,9].

Thiazole decorated polymers are currently receiving significant attention among CPs due to their electron-deficient behavior. The introduction of a thiazole ring in the CPs increases their oxidative stability and ionization potential and enhances their interaction with other molecules through van der Waals forces and charge transfer behavior [10,11]. The presence of nitrogen in the thiazole ring imparts the polymers a basic nature, allowing for acid-base interactions and further enhancing charge transfer absorption [8]. Reichmanis et al. have developed a π -conjugated polymer based on thiazole and investigated the chemical sensing of protic and Lewis acids [8]. Ozkaya et al. have synthesized a thiazole-based *p-tert*butylcalix[4]arene diamine which produced C[4]-DT. They used a C[4]-DT LB fabricated sensor for the sensitive and selective detection of DCM [12]. Additionally, incorporating a benzoselenadiazole ring in the CPs promotes electron-deficient behavior and decreases the band gap of the CPs [7,13]. Moreover, the strong polarizability of Se provides an electrophilic center that allows weak interactions with other molecules [14]. The π - π interaction between the polymeric chain also accelerates

the charge carrier mobility, leading to increased sensitivity toward targeted molecules [7,15].

Today, there is significant concern about the impact of industrial development and the release of large amounts of toxic gases and volatile organic compounds (VOCs) into the environment. One particular harmful air pollutant, sulfur dioxide (SO₂), is commonly emitted from activities such as burning fossil fuels, industrial processes, motor vehicle emissions, thermal power plants, and forest fires [16,17,18,19]. Moreover, SO₂ reacts with water to form sulfurous and sulfuric acid, resulting in acidic rain. This acidic rain has a detrimental impact on agricultural productivity and the environment. The National Ambient Air Quality Standards (NAAQS) state that the acceptable safety limit for SO₂ in atmospheric air is 0.5 ppm for a duration of 3 h [20]. Exposure of even trace amounts of SO₂ for a longer time period can cause eye irritation, respiratory illnesses such as asthma, cardiovascular diseases, and even death. Excessive exposure to SO₂ decreases the level of intracellular glutathione (GSH), which in turn destroys the antioxidant defense system of the body [21]. For this reason, there is a lot of interest in developing sensitive and selective methods to detect low concentrations of SO₂ under ambient conditions. So far, various types of gas sensors have been developed for this purpose such as electrochemical sensors, fluorescence sensors, and chemiresistive sensors [16,22]. The chemiresistive sensor is widely used among different sensors due to its unique properties such as easy miniaturization, low power consumption, reliability, affordability, simplicity, and high sensitivity [23,24,25]. Therefore, researchers are motivated to develop a sensing material that can detect SO₂ at room temperature with high sensitivity and selectivity. This is important for monitoring environmental pollution and human health. [26].

In this study, we developed two types of CPs named BBTBSe and BBT through solution phase polymerization. BBTBSe is decorated with a benzoselenadiazole ring, while BBT doesn't have this decoration. Both BBTBSe and BBT CPs were fabricated on interdigitated electrodes for the purpose for detecting SO₂. The BBTBSe sensor displays high sensitivity (R_g/R_a) and selectivity towards SO₂, with a short response time of 60 s and recovery time of 70 s at room temperature. Furthermore, sensing experiments using BBTBSe and BBT were performed by varying the concentration of SO₂. The results reveal that SO₂ could be detected even at low ppm levels with a limit of detection (LOD) of 0.23 ppb. Both sensors exhibited highly selective behavior towards SO₂, distinguishing it from other interfering oxidizing and reducing gases. Moreover, both BBTBSe and BBT sensors demonstrated complete reversibility, good repeatability, and superior durability under ambient conditions.

3.2 Aims and Objectives

The aims and objectives of the current work are mentioned as follows;

(i) To synthesize a benzoselenadiazole containing monomer, denoted as BPBSe, and two conjugated polymers (CPs) in which, one is decorated with thiazole rings (BBT) and the other contains thiazole and benzoselenadiazole rings in the backbone of the polymer (BBTBSe).

(ii) To investigate the presence of thiazole rings in BBT CP and thiazole and benzoselenadiazole rings in BBTBSe CP.

(iii) To evaluate the thermal stability and surface morphology of the BPBSe, BBT, and BBTBSe.

(iv) To investigate the sensing performance of BBT and BBTBSe for detecting SO₂ at RT.

(v) To investigate the selectivity, a dynamic response at different concentrations, and repeatability of BBT and BBTBSe CPs.

(vi) To investigate the proposed sensing mechanism of the BBTBSe sensor.

3.3 Experimental Section

3.3.1 Chemicals and Methods

The chemicals and reagents were purchased commercially and used without further purification. *o*-Phenylenediamine, 4-bromobenzonitrile and copper acetate were purchased from Alfa Aesar. Selenium dioxide, potassium carbonate and potassium acetate were purchased from SRL, India and bis(pinacolato)diborane and triethylamine were purchased from Spectrochem. Bromine and 1,4-dicyanobenzene were purchased from Merck. Tetrakis(triphenylphosphine)palladium(0) and 2,5diaminobenzene-1,4-dithiol were purchased from TCI Chemicals. All the solvents used in the reactions were purchased from Merck and distilled before use by following the standard procedure. Thin layer-layer chromatography (aluminium plates coated with Merck silica gel 60 F254) was used to monitor the progress of reactions. All the intermediates and final compounds were purified using silica gel with 100-200 mesh size.

3.3.2 Synthesis of Compounds

3.3.2.1 Synthesis of Intermediates and Monomer (4,4'-benzo[c][1,2,5] selenadiazole-4,7-diyl)dibenzonitrile, BPBSe)

Scheme 3.1 Synthetic scheme of BPBSe (4,4'-benzo[c][1,2,5] selenadiazole-4,7-diyl)dibenzonitrile, 6)



3.3.2.1.1 Synthesis of benzo[c][1,2,5]selenadiazole (2)

1 g of *o*-phenylenediamine (9.2 mmol) and 1.13 g of SeO₂ (10.17 mmol) were dissolved in ethanol (10 mL) and refluxed for 4 h at 70 °C. After the completion of the reaction, ethanol was evaporated under reduced pressure. The obtained solid was dissolved in ethyl acetate and washed with 1N HCl (3 × 30 mL). The ethyl acetate layer was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure to obtain brown needles. The solid state was purified by column chromatography on silica gel (eluting with 70:30 DCM in hexane). Yield = 89% (1.5 g, 8.19 mmol). ¹H NMR (CDCl₃, 500 MHz): 7.84-7.82 (d, 2H, Se ring, *J* = 10.2 Hz), 7.46-7.44 (m, 2H, Se ring). ¹³C NMR (CDCl₃, 125 MHz): δ = 160.59, 129.48, 123.48.



3.3.2.1.2 Synthesis of 4,7-dibromobenzo[c][1,2,5]selenadiazole (3)

1 g of benzoselenadiazole (5.4 mmol) and 1.67 g of silver sulfate (5.4 mmol) were dissolved in concentrated sulphuric acid (20 mL). 1.9 g of bromine (11.9 mmol) was added to the reaction mixture under cold conditions and stirred overnight at room temperature. After the completion of the reaction, excess bromine was quenched with cold H_2O , the resulting precipitate was filtered using a Buchner funnel. The product

was extracted using ethyl acetate and the ethyl acetate solution was dried over Na₂SO₄. The solvent was evaporated under reduced pressure to obtain a golden yellow product. The crude product was purified by column chromatography on silica gel (eluting with 50:50 DCM in hexane). Yield = 54% (1.08 g, 2.93 mmol). ¹H NMR (DMSO- d_6 , 500 MHz): 7.8 (s, 2H, Se ring). ¹³C NMR (DMSO- d_6 , 125 MHz): δ = 156.63, 132.21, 116.45.

- 7.80





3.3.2.1.3 Synthesis of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)benzonitrile (5)

500 mg of 4-bromobenzonitrile (2.74 mmol) was dissolved in dried tetrahydrofuran (THF) and purged with nitrogen gas for 10 min. 539 mg of potassium acetate (5.49 mmol) was added to the reaction and stirred for 15 min under an inert atmosphere. 1.04 g of bis(pinacolato)diboron (4.1 mmol) was added to the above mixture and allowed to stir. 158 mg tetrakis(triphenylphosphine)palladium(0) (5 mol%) was added and the reaction mixture was allowed to reflux under an inert atmosphere at 90 °C for 24 h. After the completion of the reaction, THF was evaporated under reduced pressure and diluted with dichloromethane (DCM). The mixture was passed through celite and the filtrate was taken in a separating funnel and washed with water (3×30 mL). The DCM layer was dried over Na₂SO₄ and evaporated under reduced pressure to obtain a white solid compound. Yield = 60% (375 mg, 1.64 mmol). ¹H NMR $(CDCl_3, 500 \text{ MHz})$: 7.89-7.87 (d, 2H, H of Ph, J = 8.15 Hz), 7.64-7.63 (d, 2H, H of Ph, J = 8.25 Hz), 1.35 (s, 12H, H of CH₃). ¹³C NMR $(CDCl_3, 125 \text{ MHz}): \delta = 135.10, 131.15, 118.88, 114.55, 84.51, 29.70,$ 24.87.









3.3.2.1.4 Synthesis of 4,4'-benzo[c][1,2,5]selenadiazole-4,7-diyl) dibenzonitrile (BPBSe, 6)

500 mg of 4,7-dibromo-2,1,3-benzoselenadiazole (3, 1.47 mmol), 1,01 g of 4-(4,4,5,5-tetramethyl-1,2,3-dioxaborolan-2-yl)benzonitrile (5, 4.4 mmol) and 2 g potassium carbonate (14.7 mmol) were dissolved in toluene (15 mL) and H₂O (5 mL). The above reaction mixture was purged with nitrogen for 30 min and then, 68 mg of tetrakis(triphenylphosphine)palladium(0) (4 mol%) was added to the above mixture. The reaction was refluxed and stirred under an inert atmosphere for 48 h at 100 °C. The toluene was evaporated under reduced pressure. The product was passed through celite and extracted using DCM and washed with deionized water (3 \times 30 mL). The DCM layer was dried over Na₂SO₄ and the solvent was evaporated under reduced pressure to obtain a yellow solid compound. Yield = 65% (370 mg, 0.96 mmol). ¹H NMR (CDCl₃, 500 MHz): 7.79-7.77 (d, 4H, Ph ring, J = 8.4 Hz), 7.70-7.68 (d, 4H, Ph ring, J = 8.4 Hz), 7.64 (s, 2H, CH of Se ring). ¹³C NMR (CDCl₃, 125 MHz): $\delta = 157.26, 132.91, 132.16, 127.95,$ 116.55, 112.68.



Figure 3.7 ¹H NMR spectrum (500 MHz, CDCl₃) of 6.



Figure 3.8 ¹³C NMR spectrum (125 MHz, CDCl₃) of **6**.

3.3.2.2 Synthesis of BBTBSe

A mixture of 150 mg of 4,4'-(benzo[c][1,2,5]selenadiazole-4,7diyl)dibenzonitrile (**6**, 0.38 mmol), 7.7 mg of copper acetate (0.58 mmol) and 78 mg of triethylamine (0.77 mmol) were added to ethanol. The resulting solution was stirred for 10 min and then 143 mg of 2,5diaminobenzene-1,4-dithiol (7, 0.58 mmol) was added to the above solution and the mixture allowed to stir for 72 h at 70 °C (Scheme 3.2). After the completion of the reaction, the solution was filtered and washed with water and ethanol. The resulting product was dried in an oven at 60 °C for 8 h to obtain black powder.

Scheme 3.2 Synthetic scheme of BBTBSe and BBT CPs



3.3.2.3 Synthesis of BBT

A mixture of 200 mg of 1,4-dicyanobenzene (1.56 mmol), 31 mg of copper acetate (0.58 mmol), and 158.9 mg of triethylamine (0.77 mmol) were added to ethanol. The resulting solution was stirred for 10 min and 382 mg of 2,5-diaminobenzene-1,4-dithiol (0.58 mmol) was added to the above solution and allowed to stir for 72 h at 70 °C (**Scheme 3.2**). After the completion of the reaction, the resulting solution was filtered and washed with water and ethanol, and dried in an oven at 60 °C for 8 h.

3.3.3 Characterization Techniques

¹H and ¹³C NMR spectra of the intermediates and final compound were recorded on a Bruker AV 500 MHz instrument. The solvents used were CDCl₃ and DMSO-*d*₆, with TMSA as an internal standard. The chemical shifts (δ) were expressed in ppm relative to TMS. FTIR spectra of precursors and polymers were recorded on a Bruker (Tensor-27) FT-IR spectrophotometer. The crystalline nature of the samples was studied by Empyrean, Malvern Panalytical X-ray diffractometer with Cu-K_a radiation ($\lambda = 1.54$ Å) in the 2 θ range of 5°–60°. The ¹³C CP-MAS NMR spectrum was recorded using a solid state NMR spectrometer (500 MHz Bruker Advance Neo). Thermogravimetric analysis (TGA) was performed using a Mettler Toledo Thermal Analyzer with a heating rate of 10 °C/min, heating from 25 °C to 800 °C under a nitrogen atmosphere. The surface area and pore size of the precursor and conjugated polymers were analyzed using the Quantachrome Autosorb iQ2. The surface morphology was investigated using FE-SEM (Supra55 Zeiss). Further, high-resolution transmission electron microscopy analysis was performed using the Field Emission Gun-Transmission Electron Microscope 300 kV (model no Tecnai G2, F30), operated at a of 300 kV. X-ray photoelectron spectroscopy (XPS) voltage measurements were carried out to determine the surface chemical state and elemental composition of the conjugated polymers by Thermo Fisher Scientific NEXA Surface analyzer.

3.3.4 Device Fabrication and SO₂ Sensing Evaluation

Scheme 3.3 Schematic representation of fabrication of CPs on interdigitated electrodes (IDEs)



The as-synthesized BBTBSe powder was dispersed in 1 mL of ethanol and 10 μ L nafion (used as a binder) to form a paste. This paste was dropcasted onto platinum IDEs and the fabricated device was heated in a hot air oven at 70 °C for 12 h to enhance the stability of the sensing layer (**Scheme 3.3**). The same process was repeated for the fabrication of BPBSe and BBT. The complete information on the sensing instrument, which is used for the SO₂ sensing experiment, has already been reported [27]. All the SO₂ sensing experiments were carried out under ambient conditions. The SO₂ sensing response is a function of resistance and the change in the resistance was measured using a Keithley source meter (2612A) at a constant voltage of 10 mV. After the stabilization of the resistance of the fabricated sensors in the environment, the targeted gas was exposed to the sensing chamber and the changes in resistance were observed. The required different concentrations of SO_2 were obtained by mixing SO_2 with synthetic air and controlling the flow rate using mass flow controllers (MFCs).

The response of the CP sensor was calculated using the equation below:

$$Response(R) = \frac{R_g}{R_a}$$
(3.1)

where, R_g and R_a are the resistance of the fabricated device in the targeted gas and air, respectively. Generally, the response/recovery time is expressed as the time required for achieving 90% of the resistance change after exposing or removing the targeted gas from the sensing chamber. The cylinders of gases H₂S, NO₂, CO, SO₂, NH₃, SO₂, and CO₂ with a purity of 99.9% of known concentration were purchased from air gas material and used to attain different gaseous environments inside the chamber. Further, low concentrations of SO₂ were achieved by mixing SO2 with synthetic air in the mixing chamber with pre-defined gas flow rates controlled by mass flow controllers. To investigate the repeatability behavior of the sensor, the fabricated device was exposed to SO₂ gas for 3 consecutive cycles, and a change in the resistance was observed. The different levels of relative humidity (RH) were achieved by using the saturated solutions of magnesium nitrate Mg(NO₃)₂, sodium chloride (NaCl), potassium chloride (KCl), and potassium sulfate (K₂SO₄) to obtain 57, 75, 84, and 97% RH, respectively.

The gas sensitivity is utilized to establish the limits of detection (LOD) and quantification (LOQ). The LOD represents the minimum detectable SO_2 concentration by the sensor, while the LOQ represents the lowest amount of SO_2 that can be precisely and accurately quantitatively detected [28]. The LOD and LOQ values are determined by:

$$LOD = \frac{3 \times SD}{\sigma}$$
(3.2)

$$LOQ = \frac{10 \times SD}{\sigma}$$
(3.3)

where, *SD* represents the standard deviation of sensor response values obtained in the presence of air, while σ represents the slope of the linear portion of the calibrated curve.

3.4 Results and Discussion

The synthesized BPBSe (monomer), BBT CP, and BBTBSe CP were characterized using various techniques. **Figure 3.9a** displays the PXRD pattern of 2,5-diaminobenzene-1,4-dithiol, BPBSe, and BBTSe, while **Figure 3.9b** illustrates the PXRD spectrum of 1,4-dicyanobenzene and BBT. The PXRD patterns of 2,5-diaminobenzene-1,4-dithiol, BPBSe, and 1,4-dicyanobenzene exhibited sharp peaks, corresponding to their high crystalline nature [28,29]. On the other hand, the PXRD patterns of BBT and BBTBSe showed sharp peaks with a broad hump, suggesting a low crystallinity for both CPs [30].



Figure 3.9 (a) PXRD spectrum of 2,5-diaminobenzene-1,4-dithiol, BPBSe and BBTBSe. (b) PXRD spectra of 1,4-dicyanobenzene and BBT. (c) FTIR spectrum of 2,5-diaminobenzene-1,4-dithiol, BPBSe and

BBTBSe and (d) FTIR spectra of 2,5-diamino-1,4-benzenedithiol, 1,4-dicyanobenzene and BBT.

FT-IR analysis was performed to ascertain the functional groups in BBTBSe and BBT. The FT-IR spectra of 2,5-diaminobenzene-1,4-dithiol showed characteristic peaks at 2564, 1280, and 1100 cm⁻¹, which correspond to stretching frequencies of S-H, C-N and C-S, respectively [31]. Additionally, the FT-IR spectra of BPBSe exhibited a signal at 2227 cm⁻¹, indicating the stretching frequency of CN [32]. The disappearance of characteristics peaks in the FT-IR spectra of BBTBSe at 2564 and 2227 cm⁻¹ and the appearance of peaks at 1594, 1210, and 860 cm⁻¹, which correspond to the stretching frequencies of C=N-C, N-C-S, and C-S-C, respectively, reveal the formation of thiazole ring in BBTBSe CP (Figure 3.9c) [33,34]. Similarly, the FT-IR spectrum of BBT shows the disappearance of characteristics peaks at 2564 and 2232 cm⁻¹ and the appearance of signals at 1602, 1220, and 834 cm⁻¹, which correspond to the stretching frequency of C=N-C, N-C-S, and C-S-C, respectively, revealing the formation of a thiazole (Figure 3.9d) [33,34,35]. It was observed that CN and SH stretching frequency peaks disappeared, and new C=N-C, N-C-S, and C-S-C stretching frequency peaks appeared in BBTBSe and BBT. These changes are ascribed to the successful formation of the thiazole ring in the CPs.

Moreover, the successful formation of BBTBSe and BBT was studied using ¹³C CP-MAS NMR and ¹H NMR, respectively. The peaks at δ 154.28 and 141.52 ppm correspond to C=N and C–N, respectively [36,37]. The signals at δ 131.25, 125.44, and 110.06 ppm are attributed to other aromatic carbons of the polymer (**Figure 3.10a**) [38]. The results of ¹³C CP–MAS NMR corroborate the findings of FTIR spectra, providing unambiguous evidence of the successful formation of BBTBSe. The ¹H NMR data of the synthesized BBT matches completely with the previously reported NMR of BBT (**Figure 3.10b**). The peak at δ 8.09 ppm corresponds to the benzene ring, while the peaks at δ 7.97 and 7.87 ppm are attributed to the benzothiazole ring. The signals at δ 7.45
and 7.38 ppm are attributed to the terminal benzene ring and the signal at δ 6.86 ppm is attributed to the terminal benzothiazole ring of the polymer [39].



8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 **Figure 3.10** (a) ¹³C CP-MAS NMR of BBTBSe and (b) ¹H NMR (500 MHz, DMSO- d_6) spectrum of BBT.

The porosities of BPBSe, BBTBSe, and BBT were calculated using N₂ sorption isotherm (**Figure 3.11a-3.11c**). The BET surface area of BPBSe, BBTBSe, and BBT were found to be 9.809 m²/g, 17.9 m²/g, and 18.9 m²/g, respectively. Moreover, the pore size of BPBSe, BBTBSe, and BBT was calculated using the NL-DFT method, and the values were determined to be 0.019, 0.057, and 0.057 cm³/g, respectively. The surface area of BBTBSe and BBT is almost similar and higher than that of BPBSe.

The thermal stability of BPBSe, BBTBSe, and BBT was studied using TGA analysis (**Figure 3.11**). The BBTBSe showed a weight loss of 8.5% up to 260 °C, which can be attributed to the removal of entrapped water and residual solvents. The TGA curve then sharply declined between 260 - 610 °C, resulting in a total weight loss of 90% (**Figure 3.11d**). BPBSe,

on the other hand, showed a weight loss of 9% up to 250 °C, which can be attributed to the loss of water molecules and residual solvents. Then, a sudden decrease in weight loss of 91% was observed in the range of 317-470 °C. At 470 °C, all of the monomer was completely lost. The TGA graph of BBT exhibits two weight losses (**Figure 3.11e**). The BBT remains stable up to 133 °C, but above this temperature, CP starts to degrade. The weight losses of 58% and 33% were observed between 133 and 196 °C, and between 196 to 507 °C, respectively. These observations correspond that BBTBSe has higher thermal stability compared to BPBSe and BBT [40,41]. Therefore, the TGA results reveal that all the fabricated sensors are thermally stable enough to work as sensing materials at 25 °C.



Figure 3.11 N_2 adsorption/desorption isotherm curves of (a) BPBSe (b) BBTBSe, and (c) BBT (Inset pore diameter curve of (a) BPBSe, (b) BBTBSe, and (c) BBT, calculated by NL-DFT method). (d) Thermogravimetric analysis of BPBSe and BBTBSe and (e) thermogravimetric analysis of BBT to investigate the thermal stability of the curve.

The surface morphologies of BPBSe, BBTBSe, and BBT were observed using the FE-SEM technique. The FE-SEM images of BPBSe show a rod-like morphology with a rough surface (**Figure 3.12a**) [42]. On the other hand, the FE-SEM images of BBTBSe and BBT show a coral-reeflike morphology (**Figure 3.12b and 3.12c, respectively**) [43]. HR-TEM analysis was performed to corroborate the morphology of BBT and BBTBSe, which also showed a coral reef-like morphology for both CP (**Figure 3.12d and 3.12e**). The difference in microstructure or morphology of BPBSe from BBT and BBTBSe CP could potentially be the self-aggregation of molecules and the van der Waals interaction between conjugated polymer chains. Moreover, increasing the number of conjugated units in the backbone of the CP induces interchain interactions (π - π stacking) within the conjugated polymer. These interactions alter the microstructure of the BPBSe, BBT, and BBTBSe [44,45,46].



Figure 3.12 FESEM images of (a) BPBSe, (b) BBTBSe, and (c) BBT. HRTEM images of (d) BBTBSe and (e) BBT.

The surface composition of the BBTBSe and BBT samples, as prepared, were analyzed using XPS. The survey spectrum of BBTBSe illustrates the presence of Se, S, N, and C (Figure 3.13a). The binding energy peak at 56.6 eV is attributed to $3d_{5/2}$ of the benzoselenadiazole ring in BBTBSe CP [47]. This high-resolution XPS spectrum of Se shows the presence of Se and N-Se-N bonds in BBTBSe CP (Figure 3.13b) [48,49]. The deconvoluted S spectrum consists of two binding energy peaks at 163.1 and 164.3, which are ascribed to C-S-C. This further confirms the successful formation of the thiazole ring (Figure 3.13c) [50,51]. The deconvoluted XPS spectrum of N exhibits 2 peaks at 398.7 400.7 eV, and indicating the binding energies of C=N of

benzoselenadiazole and C–N–C, respectively (**Figure 3.13d**) [48,52]. Five deconvoluted peaks were observed for C1s centered at 288.2, 286.4, 286, 284.8, and 284.4 eV, indicating C–N, N–C–S, C–S, C–C, and C=C bonds, respectively (**Figure 3.13e**) [53].



Figure 3.13 (a) XPS survey spectrum of BBTBSe. The deconvolute spectrum of (b) Se, (c) S 1s, (d) N 1s, and (e) C 1s in BBTBSe. (f) XPS survey spectrum of BBT. The deconvoluted spectrum of (g) S 1s, (g) N 1s, and (i) C 1s present in BBT.

The survey spectrum of BBT illustrates the presence of S, N, and C (**Figure 3.13f**). The deconvolute XPS spectrum of S 2p exhibits three predominant peaks at 164, 163.1, and 161.5 eV, indicating the presence of C–S and C–S–C bonds (**Figure 3.13g**) [50,51]. The deconvoluted XPS spectrum of N 1s displays two binding energy peaks at 400 and 398.6 eV, which are attributed to C–N–C and C=N bonds, respectively (**Figure 3.13h**) [48,52]. As displayed in **Figure 3.13i**, the C 1s spectrum exhibits peaks at 288.2, 286, 284.8, and 284.2 eV, which are ascribed to C–N, N–C–S, C–S, and C=C, respectively [53]. The deconvoluted XPS spectrum of nitrogen exhibited slightly higher binding energies in

BBTBSe than BBT. This suggests a different chemical environment, including variation in chemical bonding, structure, and chemical state around nitrogen atoms [54,55]. However, the electronegativity difference among carbon, sulfur, and selenium also impacts the binding energies of nitrogen, highlighting the different chemical interactions and bonding of nitrogen [47]. The XPS spectra indicate the presence of Se, S, N, and C elements in BBTBSe CP and S, N, and C elements in BBT CP.

3.4.1 SO₂ Sensing Performance

The *I-V* analysis of BBTSe and BBT sensors were investigated in the absence of SO_2 at a constant voltage range of -5 to 5 V (**Figure 3.14a-3.14b, respectively**). The *I-V* graph of BBTBSe shows a nonlinear nature, indicating a Schottky contact between BBTBSe and platinum electrode [27,56]. On the other hand, the *I-V* graph of BBT shows a linear curve, indicating an ohmic nature [57,58]. The current observed for both sensors was in the nanoampere range, indicating that they are low-power device sensors.



Figure 3.14 Current-Voltage (*I-V*) analysis of (a) BBTBSe and (b) BBT fabricated sensors.

The response values of BBTBSe, BPBSe, and BBT sensors to 100 ppm SO₂ at 25 °C were compared (**Figure 3.15a**). The graph clearly shows that BBTBSe exhibits a significantly higher response compared to BPBSe and BBT. The BBTBSe sensor exhibits a 4.3-fold higher response (R_g/R_a) of 199.4 compared to BBT ($R_g/R_a = 43.5$). All of the sensors show complete recovery to their base resistance after the exposure of SO₂ in the sensing chamber was stopped, but BBTBSe and

BBT show a low recovery time compared to BPBSe. One possible reason is that the higher surface area and pore size of BBTBSe and BBT provide proper sorption channels, which in turn decrease the response/recovery times of BBTBSe and BBT. The transient response/recovery graph indicates that BBTBSe exhibits a response of 199.4, with a rapid response/recovery time of 60/70 s (**Figure 3.15b**). This may be due to the extended π - π conjugation in the polymer, which enhances carrier transport [59].



Figure 3.15 (a) Response of BPBSe, BBT, and BBTBSe sensors to 100 ppm SO₂. (b) Single transient curve of response/recovery time of BBTBSe sensor to 100 ppm SO₂. (c) Selectivity of BBTBSe and BBT sensors for various gases. (d) Dynamic response for BBTBSe and BBT sensors for different concentrations of SO₂ (1 to 100 ppm). (e) The relation between SO₂ concentration (1 to 50 ppm) and the response of

BBTBSe sensor and (f) the relation between SO_2 concentration (1 ppm to 50 ppm) and the response of BBT sensor at 25 °C.

Selectivity is one of the crucial parameters in the obscure environment. Therefore, the responses of BBTBSe and BBT sensors towards different reducing and oxidizing gases were investigated under ambient conditions (Figure 3.15c). The BBTBSe sensor shows response values of 18.6, 26, 199.4, 25, 37.5, and 21 to interfering gases such as H₂S (100 ppm), NO₂ (100 ppm), SO₂ (100 ppm), CO (200 ppm), CO₂ (500 ppm), and NH₃ (500 ppm), respectively. The BBT sensor responses to different interfering gases such as H₂S (100 ppm), NO₂ (100 ppm), SO₂ (100 ppm), CO (200 ppm), CO₂ (500 ppm), and NH₃ (500 ppm) with the response values of 9.6, 5.8, 45.7, 7.3, 4.3, and 2.3, respectively. The selectivity factors of the BBTBSe sensor for 100 ppm SO₂ are calculated to be $S_{SO2}/S_{H2S} = 10.7$, $S_{SO2}/S_{NO2} = 7.6$, $S_{SO2}/S_{CO} = 7.97$, $S_{SO2}/S_{CO2} = 5.3$ and $S_{SO2}/S_{NH3} = 9.49$ [60]. The selectivity factors of the BBT sensor for 100 ppm SO₂ are calculated to be $S_{SO2}/S_{H2S} = 4.76$, $S_{SO2}/S_{NO2} = 7.87$, $S_{SO2}/S_{CO} = 6.2$, $S_{SO2}/S_{CO2} = 10.6$ and $S_{SO2}/S_{NH3} = 19.86$ [60]. It is evident that BBTBSe and BBT sensors exhibit a significantly higher response to SO₂ compared to other oxidizing and reducing gases, indicating their highly selective behavior towards SO₂ gas.

Afterward, the dynamic sensing performance of BBTBSe and BBT sensors at different concentrations of SO₂ were investigated at 25 °C (**Figure 3.15d**). As the concentration of SO₂ increases from 1 to 100 ppm, the response values of BBTBSe and BBT sensors increase from 11.3 to 199.4 and 6.25 to 45.7, respectively. The graph clearly shows that both sensors respond linearly to increasing concentration. The LOD and LOQ values for BBTBSe are found to be 0.23 and 0.76 ppb, (**Figure 3.15e**) respectively, whereas for BBT, the values of LOD and LOQ are found to be 1.7 and 5.6 ppb, respectively (**Figure 3.15f**). Moreover, the BBTBSe sensor exhibits an excellent response even at low concentrations, with a response value (R_g/R_d) of 11 at 1 ppm of SO₂. Both the BBTBSe and BBT sensors display complete recovery at all

concentrations, indicating excellent reversibility behavior after every cycle.



Figure 3.16 (a) Response of BBT and BBTBSe sensors towards 100 ppm SO₂ under different RH (57% to 97% RH) conditions. (b) Repeatability curve of BBTBSe and BBT sensor towards SO₂ and (c) durability test of BBTBSe and BBT sensors towards 100 ppm SO₂.

The sensing performance of the BBT and BBTBSe sensors to detect 100 ppm of SO₂ was investigated under varying levels of relative humidity (RH) at 25 °C (**Figure 3.16a**). When exposed to 100 ppm of SO₂, the BBT sensor showed responses of 39, 33, 25, and 18 under RH levels of 57%, 75%, 84%, and 97%, respectively. In contrast, the BBTBSe sensor displayed responses of 182, 154, 123, and 106 under the same RH conditions of 57%, 75%, 84%, and 97%, respectively, upon exposure to 100 ppm of SO₂. As the relative humidity (RH) increases, the response of both BBT and BBTBSe sensors to SO₂ decreases. The low response under humid conditions might be due to water molecules competing with SO₂ molecules to occupy the sensor's active sites, which in turn decreases the number of available active sites for SO₂ gas molecules on

the sensor's surface. [27,56]. Consequently, the response of both the BBT and BBTBSe sensors to SO₂ decreases significantly under high RH conditions. Further, reproducibility and stability are important factors for the practical application of the device. **Figure 3.16b** displays the response/recovery curve of BBTBSe and BBT sensors to 100 ppm of SO₂ for 3 consecutive cycles. The results illustrate that there were no significant fluctuations in the response values when SO₂ molecules were injected or withdrawn from the sensing chamber. This result proves that BBTBSe and BBT sensors exhibit excellent repeatability under ambient conditions. Further, a monthly aging analysis was performed for 2 months, every fifth day (**Figure 3.16c**). Both BBTBSe and BBT sensors did not show any noticeable change in their response to 100 ppm of SO₂, indicating the excellent stability of the sensors.

Finally, the sensing performance of BBTBSe towards SO_2 gas was compared with the materials that have been previously reported. It is evident from **Table 3.1** that BBTBSe exhibits a significantly high response and can be used as an excellent sensing material for detecting SO_2 , with a fast response/recovery time under ambient conditions.

 Table 3.1 Comparison of sensing performance of BBTBSe sensor with

 other reported materials towards SO2

S.	Material	Respo	Concentrati	Tempera	Reference
No.		nse	on (ppm)	ture (°C)	
1.	AuNPs-	10.4	20	200	25
	SnO ₂				
2.	NiO/SnO ₂	56	500	180	61
3.	Ag/PANI/S	20	50	20	62
	nO ₂				
4.	ZnO-	156	70	300	18
	MWCNT				
	(15:1)				
5.	Ag/Ag ₂ S/S	10	100	180	63
	-SnO ₂				

Chapter 3

6.	Ru/Al ₂ O ₃ /	65%	100	350	64
	ZnO				
7.	CBD of	93%	70	300	65
	ZnO				
8.	SnO ₂ /MoS ₂	16	20	RT	66
9.	BBTBSe	199.4	100	25	This work

3.4.2 SO₂ Sensing Mechanism

However, the mechanism by which BBTBSe senses SO₂ is not well understood, and this will be an important topic for future research. The sensing mechanism of BBTBSe conjugated polymer for SO₂ at 25 °C could be explained on the basis of the interaction between SO₂ and CP (Scheme 3.4). The presence of nitrogen (N) in the benzoselenadiazole and thiazole rings of BBTBSe increases the number of active sites on its surface for the adsorption of SO₂. The lone pairs of N in the benzoselenadiazole and thiazole rings are transferred to the S atom of SO₂ which has a partial positive charge. This transfer leads to a dipoledipole interaction. Subsequently, the donation of lone pairs to SO₂ causes an electron deficiency in the C=N bond, which weakens the conjugation (delocalization of electrons) in the backbone of the CP and decreases the charge carrier density of the CP [67]. Consequently, an increase in resistance was observed for the CP sensor when exposed to SO₂. This led to the calculation of the response value of the sensors. Moreover, this weak interaction not only enhances the adsorption/desorption process, but also decreases the adsorption/desorption time of SO₂ on the surface of BBTBSe. Consequently, the response and recovery time of the BBTBSe sensor decrease upon exposure to SO₂ [68].

In addition, there are plenty of N present in the BBTBSe ring, which highly increases its basicity [69]. This allows it to form a temporary complex with SO₂ molecules through weak Lewis acid-base interaction [70]. The physisorption of SO₂ on the BBTBSe surface results in a significant change in the resistance of the sensor. As a result, the response of the BBTBSe sensor to SO₂ gas was calculated. The sensor exhibits complete recoverable behavior due to the complete desorption of SO₂ from the surface of BBTBSe [17]. The adsorption of acidic gas can be increased by increasing the basicity of the conjugated polymer. This can be achieved by introducing more N into the polymer as nitrogen contains lone pair of electrons, which act as basic active sites for the interaction with acidic gases. However, the lone pair of electrons of nitrogen in BBTBSe and BBT is not strong enough to chemically bind with SO₂. Instead, the nitrogen present in BBTBSe and SO₂ are bonded through a weak physical interaction. Therefore, these weak interactions accelerate the complete desorption of SO₂ molecules from the polymer surface without much difficulty [71].

Scheme 3.4 Interaction of BBTBSe with SO₂ molecules



The lower response of the BBT sensor to SO_2 could be due to lower N content. Consequently, there are fewer nitrogen lone pairs available in BBT that interact with SO_2 gas molecules. This leads to a smaller change in resistance [72,73]. As a result, the BBT sensor exhibits a lower response. Reversibility is an essential criterion for evaluating the detection of SO_2 gas. The complex formed by a very weak acid-base interaction can be easily demolished by passing synthetic air through the chamber. Therefore, both the BBTBSe and BBT sensors exhibit

complete reversible behavior in sensing SO_2 [70,71]. The results discussed above suggest that the BBTBSe could be used as a facile, inexpensive, highly sensitive, and selective sensing material for detecting SO_2 at room temperature. This can be beneficial for monitoring environmental pollution and human health. However, the parameters which affect the sensing performance of the sensing material are very complex.

3.5 Conclusion

In summary, we have successfully synthesized BPBSe, BBTBSe CP, and BBT CP using a simple solution-phase method. The introduction of benzoselenadiazole ring in the CP significantly enhanced the sensing performance for SO₂ gas as compared to BBT CP. The BBTBSe sensor showed a 4.3 times higher response ($R = R_g/R_a$) of 199.4 with a fast response/recovery time of 60/70 s, in contrast to BBT (R = 45.7%). Furthermore, the response of BBTBSe to SO₂ gas increased in a linear manner within a concentration range of 1 to 50 ppm. The LOD and LOQ values for the BBTBSe sensor were found to be 0.23 and 0.76 ppb, respectively. More significantly, BBTBSe exhibited high selectivity, consistent repeatability, complete recovery, and superior durability for 60 days. Overall, the BBTBSe sensor exhibited an excellent response with a lower LOD value, suggesting that the BBTBSe can be used as a promising sensing material for monitoring human health and environmental pollution, especially in ambient conditions.

3.6 References

- Yang J., Kang F., Wang X., Zhang Q. (2022), Design Strategies for Improving the Crystallinity of Covalent Organic Frameworks and Conjugated Polymers: A Review, Mater. Horizons, 9, 121– 146 (DOI: 10.1039/d1mh00809a).
- Ye S., Lotocki V., Xu H., Seferos D. S. (2022), Group 16 Conjugated Polymers Based on Furan, Thiophene, Selenophene, and Tellurophene, Chem. Soc. Rev., 51, 6442–6474 (DOI: 10.1039/d2cs00139j).

- (3) Shin S. Y., Jang M., Cheon H. J., Go S., Yoon H., Chang M. (2022), Nanostructure-Assisted Solvent Vapor Annealing of Conjugated Polymer Thin Films for Enhanced Performance in Volatile Organic Compound Sensing, Sensors Actuators B Chem., 351, 130951 (DOI: 10.1016/j.snb.2021.130951).
- (4) Sun H., Schanze K. S. (2022), Functionalization of Water-Soluble Conjugated Polymers for Bioapplications, ACS Appl. Mater. Interfaces, 14, 20506-20519 (DOI: 10.1021/acsami.2c02475).
- (5) Zayat B., Das P., Thompson B. C., Narayan S. R. (2021), In Situ Measurement of Ionic and Electronic Conductivities of Conductive Polymers as a Function of Electrochemical Doping in Battery Electrolytes, J. Phys. Chem. C, 125, 7533–7541 (DOI: 10.1021/acs.jpcc.0c08934).
- (6) Wang Z., Lin H., Zhang M., Yu W., Zhu C., Wang P., Huang Y., Lv F., Bai H., Wang S. (2023), Water-Soluble Conjugated Polymers for Bioelectronic Systems, Mater. Horizons, 10, 1210– 1233 (DOI: 10.1039/d2mh01520j).
- Göker S., Sarigül H., Toppare L. (2020), Tailoring Optoelectronic Properties of Thieno[3,2-b]Thiophene Comprising Homopolymers via Electron Acceptor Moieties: Thienopyrrolodione, 2,1,3-Benzoselenadiazole, Isoindigo, J. Electroanal. Chem., 873, 114372 (DOI: 10.1016/j.jelechem.2020.114372).
- (8) Yuan Z., Qu Q., Hamrock K., Buckley C., Zhang G., Reichmanis E. More Than Another Halochromic Polymer: Thiazole-Based Conjugated Polymer Transistors for Acid-Sensing Applications, ACS Appl. Polym. Mater., 2, 5898–5906, (DOI: 10.1021/acsapm.0c01255).
- Liu X., Zheng W., Kumar R., Kumar M., Zhang J. (2022), Conducting Polymer-Based Nanostructures for Gas Sensors, Coord. Chem. Rev., 462, 214517 (DOI: 10.1016/j.ccr.2022.214517).
- (10) Attar S., Yang R., Chen Z., Ji X., Comí M., Banerjee S., Fang L., Liu Y., Al-Hashimi M. (2022), Thiazole Fused S, N-Heteroacene Step-Ladder Polymeric Semiconductors for Organic Transistors,

Chem. Sci., 13, 12034–12044 (DOI: 10.1039/d2sc04661j).

- (11) Yang K., Chen Z., Wang Y., Guo X. (2023), Alkoxy-Functionalized Bithiophene/Thiazoles: Versatile Building Blocks for High-Performance Organic and Polymeric Semiconductors, Accounts Mater. Res., 4, 237-250 (DOI: 10.1021/accountsmr.2c00237).
- (12) Durmaz M., Acikbas Y., Bozkurt S., Capan R., Erdogan M., Ozkaya C. (2021), A Novel Calix[4]Arene Thiourea Decorated with 2-(2-Aminophenyl)Benzothiazole Moiety as Highly Selective Chemical Gas Sensor for Dichloromethane Vapor, ChemistrySelect, 6, 4670–4676 (DOI: 10.1002/slct.202100631).
- (13) Ye F., Liu Y., Chen J., Liu S. H., Zhao W., Yin J. (2019), Tetraphenylene-Coated Near-Infrared Benzoselenodiazole Dye: AIE Behavior, Mechanochromism, and Bioimaging, Org. Lett., 21, 7213–7217 (DOI: 10.1021/acs.orglett.9b02292).
- Jadhav R. G., Kumar A., Kumar S., Maiti S., Mukherjee S., Das A. K. (2020), Benzoselenadiazole-Based Conjugated Molecules: Active Switching Layers with Nanofibrous Morphology for Nonvolatile Organic Resistive Memory Devices, Chem Plus Chem, 85, 910–920 (DOI: 10.1002/cplu.202000229).
- (15) Chen M., Cao W., Wang J., Cai F., Zhu L., Ma L., Chen T. (2022), Selenium Atom-Polarization Effect Determines TrxR-Specific Recognition of Metallodrugs, J. Am. Chem. Soc., 144, 20825–20833 (DOI: 10.1021/jacs.2c08802).
- (16) You X., Wu J., Chi Y. (2019), Superhydrophobic Silica Aerogels Encapsulated Fluorescent Perovskite Quantum Dots for Reversible Sensing of SO₂ in a 3D-Printed Gas Cell, Anal. Chem., 91, 5058–5066 (DOI: 10.1021/acs.analchem.8b05253).
- (17) Cui G., Liu J., Lyu S., Wang H., Li Z., Wang J. (2019), Efficient and Reversible SO₂ Absorption by Environmentally Friendly Task-Specific Deep Eutectic Solvents of PPZBr+Gly, ACS Sustain. Chem. Eng., 7, 14236–14246 (DOI: 10.1021/acssuschemeng.9b03245).
- (18) Septiani N. L. W., Saputro A. G., Kaneti Y. V., Maulana A. L.,

Fathurrahman F., Lim H., Yuliarto B., Nugraha, Dipojono H. K., Golberg D., Yamauchi Y. (2020), Hollow Zinc Oxide Microsphere-Multiwalled Carbon Nanotube Composites for Selective Detection of Sulfur Dioxide, ACS Appl. Nano Mater., 3, 8982–8996 (DOI: 10.1021/acsanm.0c01707).

- (19) Aranthady C., Jangid T., Gupta K., Mishra A. K., Kaushik S. D., Siruguri V., Rao G. M., Shanbhag G. V., Sundaram N. G. (2021), Selective SO₂ Detection at Low Concentration by Ca Substituted LaFeO₃ Chemiresistive Gas Sensor: A Comparative Study of LaFeO₃ Pellet vs Thin Film, Sensors Actuators, B Chem., 329, 129211 (DOI: 10.1016/j.snb.2020.129211).
- (20) Yin X., Wu H., Dong L., Li B., Ma W., Zhang L., Yin W., Xiao L., Jia S., Tittel F. K. (2020), Ppb-Level SO₂ Photoacoustic Sensors with a Suppressed Absorption-Desorption Effect by Using a 7.41 Mm External-Cavity Quantum Cascade Laser, ACS Sensors, 5, 549–556 (DOI: 10.1021/acssensors.9b02448).
- (21) Jing C., Wang Y., Song X., Li X., Kou M., Zhang G., Dou W., Liu W. (2023), Dual-Fluorophore and Dual-Site Multifunctional Fluorescence Sensor for Visualizing the Metabolic Process of GHS to SO₂ and the SO₂ Toxicological Mechanism by Two-Photon Imaging, Anal. Chem., 95, 1376–1384 (DOI: 10.1021/acs.analchem.2c04333).
- Maiti S., Mandal B., Sharma M., Mukherjee S., Das A. K. (2020),
 A Covalent Organic Polymer as an Efficient Chemosensor for Highly Selective H₂S Detection through Proton Conduction, Chem. Commun., 56, 9348–9351 (DOI: 10.1039/d0cc02704a).
- (23) Ye X., Ge L., Jiang T., Guo H., Chen B., Liu C., Hayashi K.
 (2022), Fully Inkjet-Printed Chemiresistive Sensor Array Based on Molecularly Imprinted Sol-Gel Active Materials, ACS Sensors, 7, 1819–1828 (DOI: 10.1021/acssensors.2c00093).
- (24) Li W., Lefferts M. J., Armitage B. I., Murugappan K., Castell M.
 R. (2022), Polypyrrole Percolation Network Gas Sensors: Improved Reproducibility through Conductance Monitoring during Polymer Growth, ACS Appl. Polym. Mater., 4, 2536–2543

(DOI: 10.1021/acsapm.1c01819).

- (25) Liu L., Liu S. (2018), Oxygen Vacancies as an Efficient Strategy for Promotion of Low Concentration SO₂ Gas Sensing: The Case of Au-Modified SnO₂, ACS Sustain. Chem. Eng., 6, 13427–13434 (DOI: 10.1021/acssuschemeng.8b03205).
- (26) Hu Y., Zheng W., Fan S., Zhang J., Liu X. (2023), Noble-Transition-Metal Dichalcogenides-Emerging Two-Dimensional Materials for Sensor Applications. Appl. Phys. Rev., 10, 031306 (DOI: 10.1063/5.0150018).
- (27) Patel C., Mandal B., Jadhav R. G., Ghosh T., Dubey M., Das A. K., Htay M. T., Atuchin V. V., Mukherjee S. (2021), S, N Co-Doped Carbon Dot-Functionalized WO₃ Nanostructures for NO₂ and H₂S Detection, ACS Appl. Nano Mater., 2, 2492-2500 (DOI: 10.1021/acsanm.1c04174).
- (28) Sharma M., Patel C., Sriram S., Mukherjee S., Das A. K. (2023), Investigating the Role of Amide to Thioamide Substitution of a Covalent Organic Polymer for the Selective Chemodetection of H₂S at Room Temperature, ACS Appl. Polym. Mater., 5, 10065-10072 (DOI: 10.1021/acsapm.3c01872).
- (29) An S., Xu Q., Ni Z., Hu J., Peng C., Zhai L., Guo Y., Liu H.
 (2021), Construction of Covalent Organic Frameworks with Crown Ether Struts, Angew. Chemie - Int. Ed., 60, 9959–9963 (DOI: 10.1002/anie.202101163).
- (30) Huang Z., Willhammar T., Zou X. (2021), Three-Dimensional Electron Diffraction for Porous Crystalline Materials: Structural Determination and Beyond, Chem. Sci., 12, 1206–1219 (DOI: 10.1039/d0sc05731b).
- (31) Lin L., Ni Y., Shang L., Sun H., Zhang Q., Zhang W., Yan Z., Zhao Q., Chen J. (2022), Atomic-Level Modulation-Induced Electron Redistribution in Co Coordination Polymers Elucidates the Oxygen Reduction Mechanism, ACS Catal., 12, 7531–7540 (DOI: 10.1021/acscatal.2c01075).
- (32) Huang W., Wang Z. J., Ma B. C., Ghasimi S., Gehrig D., Laquai F., Landfester K., Zhang K. A. I. (2016), Hollow Nanoporous

Covalent Triazine Frameworks: Via Acid Vapor-Assisted Solid Phase Synthesis for Enhanced Visible Light Photoactivity, J. Mater. Chem. A, 4, 7555–7559 (DOI: 10.1039/c6ta01828a).

- (33) Guo Y., Tang J., Henzie J., Jiang B., Xia W., Chen T., Bando Y., Kang Y. M., Hossain M. S. A., Sugahara Y., Yamauchi Y. (2020), Mesoporous Iron-Doped MoS₂/CoMo₂S₄ Heterostructures through Organic-Metal Cooperative Interactions on Spherical Micelles for Electrochemical Water Splitting, ACS Nano, 14, 4141–4152 (DOI: 10.1021/acsnano.9b08904).
- (34) Anbazhagan R., Krishnamoorthi R., Thankachan D., Van Dinh T. T., Wang C. F., Yang J. M., Chang Y. H., Tsai H. C. (2022), Fluorine-Free Superhydrophobic Covalent-Organic-Polymer Nanosheet Coating for Selective Dye and Emulsion Separation, Langmuir, 38, 4310–4320 (DOI: 10.1021/acs.langmuir.1c03492).
- (35) Bera P., Aher A., Brandao P., Debnath U., Dewaker V., Manna S. K., Jana A., Pramanik C., Mandal B., Bera P. (2022), Instigating the in Vitro Anticancer Activity of New Pyridine-Thiazole-Based Co(III), Mn(II), and Ni(II) Complexes: Synthesis, Structure, DFT, Docking, and MD Simulation Studies, J. Chem. Inf. Model., 62, 1437–1457 (DOI: 10.1021/acs.jcim.1c01280).
- (36) Feng J., Zhang Y. J., Ma S. H., Yang C., Wang Z. P., Ding S. Y., Li Y., Wang W. (2022), Fused-Ring-Linked Covalent Organic Frameworks, J. Am. Chem. Soc., 144, 6594–6603 (DOI: 10.1021/jacs.2c02173).
- (37) Zhao G., Mei Z., Duan L., An Q., Yang Y., Zhang C., Tan X., Guo H. (2023), COF-Based Single Li⁺ Solid Electrolyte Accelerates the Ion Diffusion and Restrains Dendrite Growth in Quasi-Solid-State Organic Batteries, Carbon Energy, 5, 1–13 (DOI: 10.1002/cey2.248).
- (38) Kumar S., Abdulhamid M. A., Dinga Wonanke A. D., Addicoat M. A., Szekely G. (2022), Norbornane-Based Covalent Organic Frameworks for Gas Separation, Nanoscale, 14, 2475–2481 (DOI: 10.1039/d1nr07593d).
- (39) Chen P., Ma Y., Zheng Z., Wu C., Wang Y., Liang G. (2019),

Facile Syntheses of Conjugated Polymers for Photothermal Tumour Therapy, Nat. Commun., 10, 1–10 (DOI: 10.1038/s41467-019-09226-6).

- (40) Guan C., Cai J., Liu X., Guo L. (2022), Highly Crystalline Covalent Organic Frameworks for Ratiometric Fluorescent Sensing of Trace Water in Honey and N₂ Gas, Sensors Actuators B Chem., 355, 131323 (DOI: 10.1016/j.snb.2021.131323).
- (41) Zhao Y., Liu H., Sun B. (2022), Chiral Induction in Carbazole-Conjugated Covalent Organic Frameworks: A Supersensitive Fluorescence Sensing Platform for Chiral Recognition, Sensors Actuators B Chem., 354, 131253 (DOI: 10.1016/j.snb.2021.131253).
- (42) Li Z., Chen J., Chen L., Guo M., Wu Y., Wei Y., Wang J., Wang X. (2020), Hollow Au/Polypyrrole Capsules to Form Porous and Neural Network-Like Nanofibrous Film for Wearable, Super-Rapid, and Ultrasensitive NH₃ Sensor at Room Temperature, ACS Appl. Mater. Interfaces, 12, 55056–55063 (DOI: 10.1021/acsami.0c15585).
- (43) Tan J. Z. Y., Nursam N. M., Xia F., Sani M. A., Li W., Wang X., Caruso R. A. (2017), High-Performance Coral Reef-like Carbon Nitrides: Synthesis and Application in Photocatalysis and Heavy Metal Ion Adsorption, ACS Appl. Mater. Interfaces, 9, 4540–4547 (DOI: 10.1021/acsami.6b11427).
- (44) Samanta S., Khatun S., Pradhan A. (2023), Morphology-Dependent Covalent Organic Polymers Exhibit Tunable Charge Storage Performance in Supercapacitor Application, ACS Appl. Energy Mater., 6, 11890–11896 (DOI: 10.1021/acsaem.3c01845).
- (45) Brabec C. J., Heeney M., Mc Culloch I., Nelson J. (2011), Influence of Blend Microstructure on Bulk Heterojunction Organic Photovoltaic Performance, Chem. Soc. Rev., 40, 1185– 1199 (DOI: 10.1039/c0cs00045k).
- (46) Meinhard D., Wegner M., Kipiani G., Hearley A., Reuter P., Fischer S., Marti O., Rieger B. (2007), New Nickel(II) Diimine Complexes and the Control of Polyethylene Microstructure by

Catalyst Design, J. Am. Chem. Soc., 129, 9182–9191 (DOI: 10.1021/ja070224i).

- (47) Li J., Jia J., Suo J., Li C., Wang Z., Li H., Valtchev V., Qiu S., Liu X., Fang Q. (2023), Metal-Free Covalent Organic Frameworks Containing Precise Heteroatoms for Electrocatalytic Oxygen Reduction Reaction, J. Mater. Chem. A, 11, 18349–18355 (DOI: 10.1039/d3ta03534d).
- (48) Jadhav R. G., Singh D., Mobin S. M., Das A. K. (2020), Engineering of Electrodeposited Binder-Free Organic-Nickel Hydroxide Based Nanohybrids for Energy Storage and Electrocatalytic Alkaline Water Splitting, Sustain. Energy Fuels, 4, 1320–1331 (DOI: 10.1039/c9se00483a).
- (49) Zheng N., Feng Y., Zhang Y., Li R., Bian C., Bao L., Du S., Dong H., Shen Y., Feng W. (2019), Reversible Modification of Nitrogen-Doped Graphene Based on Se-N Dynamic Covalent Bonds for Field-Effect Transistors, ACS Appl. Mater. Interfaces, 11, 24360–24366 (DOI: 10.1021/acsami.9b02989).
- (50) Wang H., Guan L., Liu J., Lei T., Xue Y., Qu Z., Jin S., Ma H., Guo Z. (2022), A Thiazolo[5,4-d]Thiazole Functionalized Covalent Triazine Framework Showing Superior Photocatalytic Activity for Hydrogen Production and Dye Degradation, J. Mater. Chem. A, 10, 16328–16336 (DOI: 10.1039/d2ta04177d).
- (51) Singh V., Kim J., Kang B., Moon J., Kim S., Kim W. Y., Byon H.
 R. (2021), Thiazole-Linked Covalent Organic Framework Promoting Fast Two-Electron Transfer for Lithium-Organic Batteries, Adv. Energy Mater., 11, 2003735 (DOI: 10.1002/aenm.202003735).
- (52) Liu G., Huang Y., Qu X., Xiao J., Yang X., Xu Z. (2016), Understanding the Hydrophobic Mechanism of 3-Hexyl-4-Amino-1, 2,4-Triazole-5-Thione to Malachite by ToF-SIMS, XPS, FTIR, Contact Angle, Zeta Potential and Micro-Flotation, Colloids Surfaces A Physicochem. Eng. Asp., 503, 34–42 (DOI: 10.1016/j.colsurfa.2016.05.028).
- (53) Liu S., Xin Z. J., Lei Y. J., Yang Y., Yan X. Y., Lu Y. B., Li C.

B., Wang H. Y. (2017), Thin Copper-Based Film for Efficient Electrochemical Hydrogen Production from Neutral Aqueous Solutions, ACS Sustain. Chem. Eng., 5, 7496–7501 (DOI: 10.1021/acssuschemeng.7b01646).

- (54) Kong X., Zhou S., Strømme M., Xu C. (2021), Redox Active Covalent Organic Framework-Based Conductive Nanofibers for Flexible Energy Storage Device, Carbon, 171, 248–256 (DOI: 10.1016/j.carbon.2020.09.003).
- (55) Guo J., Lin C. Y., Xia Z., Xiang Z. (2018), A Pyrolysis-Free Covalent Organic Polymer for Oxygen Reduction, Angew. Chemie - Int. Ed., 57, 12567–12572 (DOI: 10.1002/anie.201808226).
- (56) Tian X., Cui X., Xiao Y., Chen T., Xiao X., Wang Y. (2022), Pt/MoS₂/Polyaniline Nanocomposite as a Highly Effective Room Temperature Flexible Gas Sensor for Ammonia Detection, ACS Appl. Mater. Interfaces, 15, 9604-9617 (DOI: 10.1021/acsami.2c20299).
- (57) Sharma M., Patel C., Maiti S., Mukherjee S., Das A. K. (2021), Fabricated Chemiresistive Sensor for Detection of Ethanol Using NDICY-ZnO Nanohybrid, IEEE Sens. J., 23, 15342–15349 (DOI: 10.1109/JSEN.2023.3276771).
- (58) Yi C., Hou Y., He K., Li W., Li N., Wang Z., Yang B., Xu S., Wang H., Gao C., Wang Z., Gu G., Wang Z., Wei L., Yang C., Chen M. (2020), Highly Sensitive and Wide Linear-Response Pressure Sensors Featuring Zero Standby Power Consumption under Bending Conditions, ACS Appl. Mater. Interfaces, 12, 19563–19571 (DOI: 10.1021/acsami.0c02774).
- (59) Li P., Xu H., Liu F., Shi J., Gao X., Li J. (2023), Room-Temperature NH₃ Sensors Based on Polyaniline-Assembled Graphitic Carbon Nitride Nanosheets, ACS Appl. Nano Mater., 6, 5145-5154 (DOI: 10.1021/acsanm.2c04940).
- (60) Schütt F., Postica V., Adelung R., Lupan O. (2017), Single and Networked ZnO-CNT Hybrid Tetrapods for Selective Room-Temperature High-Performance Ammonia Sensors, ACS Appl.

Mater. Interfaces, 9, 23107–23118 (DOI: 10.1021/acsami.7b03702).

- (61) Tyagi P., Sharma A., Tomar M., Gupta V. (2017), SnO₂ Thin Film Sensor Having NiO Catalyst for Detection of SO₂ Gas with Improved Response Characteristics, Sensors Actuators, B Chem., 248, 998–1005 (DOI: 10.1016/j.snb.2017.02.168).
- (62) Xu H., Li J., Li P., Shi J., Gao X., Luo W. (2021), Highly Efficient SO₂ Sensing by Light-Assisted Ag/PANI/SnO₂ at Room Temperature and the Sensing Mechanism, ACS Appl. Mater. Interfaces, 13, 49194–49205 (DOI: 10.1021/acsami.1c14548).
- (63) Xu H., Li J., Fu Y., Li P., Luo W., Tian Y. (2020), A Covalent Organic Polymer as an Efficient Chemosensor for Highly Selective H₂S Detection through Proton Conduction. ACS Appl. Nano Mater., 3, 8075–8087 (DOI: 10.1021/acsanm.0c01533).
- (64) Liu Y., Xu X., Chen Y., Zhang Y., Gao X., Xu P., Li X., Fang J., Wen W. (2018), An Integrated Micro-Chip with Ru/Al₂O₃/ZnO as Sensing Material for SO₂ Detection, Sensors Actuators, B Chem., 262, 26–34 (DOI: 10.1016/j.snb.2018.01.156).
- (65) Yuliarto B., Ramadhani M. F., Nugraha Septiani N. L. W., Hamam K. A. (2017), Enhancement of SO₂ Gas Sensing Performance Using ZnO Nanorod Thin Films: The Role of Deposition Time, J. Mater. Sci., 52, 4543–4554 (DOI: 10.1007/s10853-016-0699-5).
- (66) He X.; Ying Z.; Wen F.; Li L.; Zheng X.; Zheng P.; Wang G.
 (2021), MoS₂-Doped Spherical SnO₂ for SO₂ Sensing under UV Light at Room Temperature, Mater. Sci. Semicond. Process., 134, 105997 (DOI: 10.1016/j.mssp.2021.105997).
- (67) Park H., Kim D. H., Ma B. S., Shin E., Kim Y., Kim T. S., Kim F. S., Kim I. D., Kim B. J. (2022), High-Performance, Flexible NO₂ Chemiresistors Achieved by Design of Imine-Incorporated n-Type Conjugated Polymers, Adv. Sci., 9, 2200270 (DOI: 10.1002/advs.202200270).
- (68) Zhang Z., Yang B., Ma H. (2021), Aliphatic Amine Decorating Metal-Organic Framework for Durable SO₂ Capture from Flue

Gas, Sep. Purif. Technol., 259, 118164 (DOI: 10.1016/j.seppur.2020.118164).

- (69) Maiti S., Chowdhury A. R., Das A. K. (2019),Benzoselenadiazole-Based Nanoporous Covalent Organic Polymer (COP) as Efficient Room Temperature Heterogeneous Catalyst for Biodiesel Production, Microporous Mesoporous Mater., 283, 39-47 (DOI: 10.1016/j.micromeso.2019.03.046).
- (70) Lee G. Y., Lee J., Vo H. T., Kim S., Lee H., Park T. (2017), Amine-Functionalized Covalent Organic Framework for Efficient SO₂ Capture with High Reversibility, Sci. Rep., 7, 1–10 (DOI: 10.1038/s41598-017-00738-z).
- (71) Lee H. J., Lee K. I., Kim M., Suh Y. W., Kim H. S., Lee H.
 (2016), Diamine-Anchored Polystyrene Resins for Reversible SO₂
 Adsorption, ACS Sustain. Chem. Eng., 4, 2012–2019 (DOI: 10.1021/acssuschemeng.5b01325).
- Tailor R., Abboud M., Sayari A. (2014), Supported Polytertiary Amines: Highly Efficient and Selective SO₂ Adsorbents, Environ. Sci. Technol., 48, 2025–2034 (DOI: 10.1021/es404135j).
- (73) Ou J. Z., Ge W., Carey B., Daeneke T., Rotbart A., Shan W., Wang Y., Fu Z., Chrimes A. F., Wlodarski W., Russo S. P., Li Y. X., Kalantar-Zadeh K. (2015), Physisorption-Based Charge Transfer in Two-Dimensional SnS₂ for Selective and Reversible NO₂ Gas Sensing, ACS Nano, 9, 10313–10323 (DOI: 10.1021/acsnano.5b04343).

TailoringNH3SensingResponsivenessthrough Amine Modification of Imine-basedNanoporous Covalent Organic Polymer

4.1 Introduction

The rapid development of industrialization and urbanization has led to the release of a large quantity of toxic gases directly into the environment. This has had a severe impact on the living environment and humans [1,2,3]. Particularly, ammonia (NH₃) is a highly toxic natural gas that generated from excessive livestock, waste discharge is ammonification, fertilizer factories, food processing, and combustion [4,5,6]. Exposure to NH₃ has severe effects on human health, such as causing coughing, respiratory damage, skin and eye irritation, and even death in cases of excessive exposure [7,8]. Furthermore, NH₃ can be used as a biomarker for liver diseases, oral cavity diseases, *helicobacter* pylori diagnosis, and hepatic encephalopathy diagnosis [9,5]. The concentration of NH₃ in the lungs of a healthy person is found to be 400-1800 ppb, while in patients affected by renal disease (late stage), it is found to be 820-14700 ppb [9]. The Occupational Safety and Health Administration (OSHA) has set a threshold limit value (TLV) of 25 ppm for NH₃ [10]. Therefore, there is a need to develop an NH₃ sensor with excellent selectivity and sensitivity, especially under ambient conditions (room temperature of approximately 25 °C and atmospheric humidity of approximately 45%).

Among the different types of gas sensors, chemiresistive sensors are widely investigated because of their easy miniaturization, inexpensive and easy handling [11,12]. Many sensors based on metal oxides (MOs) have been explored for monitoring NH₃, but these sensors have significant issues such as requiring high operating temperatures and lacking selectivity [11]. A composite of ZnWO₄/12WO₃-0.5 wt% rGO exhibited an excellent response of 10.1–20 ppm of NH₃ at a temperature of 140 °C [13]. A modified FeVO₄–SE with 20 mol% NiO showed a very good response to 100 ppm NH₃, which was operated at a temperature of 650 °C [14]. Recently, scientists have engineered nanoporous covalent organic polymers (nCOPs) to address the limitations of MO sensors employed in the detection of NH₃ gas. nCOPs have sparked a considerable attention due to their unique features, such as a large

surface area, rapid charge transfer, excellent chemical and thermal stability, redox properties, and tunable properties [15,16,17,18,19]. These properties make nCOPs a promising candidate for various applications, including energy storage, proton conduction, gas storage, drug delivery, and catalysis [16,20,21,22,23]. A nCOP with imine linkages was used as a sensing material for detecting NH₃. The fabricated sensor exhibited excellent sensitivity to NH₃ with rapid response/recovery time [24]. A triazine-based COP has been synthesized for the selective and sensitive detection of NH₃ with good reversibility [25]. Different functional groups such as triazine, amine, hydroxyl, imine, and thiophene have been incorporated into the backbone of the nCOPs, which improves the sensitivity, recovery, and selectivity towards specific targeted gas molecules [26].

Among the various functional groups, imine and amine bonds have attracted broad attention due to their diverse structural and functional properties. The nitrogen-decorated polymer exhibits the properties of Bronsted and Lewis acids [27]. Imine bonds can be easily formed and broken in a reversible manner, and the presence of imine bonds in the nCOPs provides the electrophilic behavior to the polymer's backbone [28]. The imine bonds are protected from hydrolysis through H-bonding between interlayer C-H and N-H, as these H-bonds create steric hindrance and a water-repelling environment near the imine bonds [29]. In addition, amine-functionalized nCOPs provide a large surface area and exhibit physiochemical stability [30]. The presence of amine groups in the nCOPs offers active sites that can interact with targeted gas molecules through hydrogen bonding and electrostatic interaction. Additionally, the amine groups lower the highest occupied molecular orbital (HOMO) level of the nanoporous polymer [31].

In the present report, we have reported a nanoporous covalent organic polymer with imine (nCOPI), which was subsequently reduced to amine (C–N) linkage nanoporous covalent organic polymer (nCOPA). The synthesized nCOPI and nCOPA were thoroughly characterized using various techniques. Further, both nCOPI and nCOPA were dropcasted onto intergitated electrodes (IDEs) and used them as sensing materials

for detecting NH₃ gas under ambient conditions. The sensing performances of the fabricated nCOPI and nCOPA have been investigated and also the response/recovery time. Compared to nCOPI, nCOPA exhibited 18.8 times higher response. The nCOPA sensor also showed a good linear increase in response when the concentration of NH₃ ranged from 1 to 500 ppm. The sensor has the lowest detection limit (LOD) and quantification limit (LOQ) values of 0.25 and 0.86 ppb, respectively. Its remarkable selectivity, complete reversibility, and superior NH₃ response under different relative humidities make it a promising candidate for NH₃ sensors operated at RT (~25 °C). Furthermore, a plausible mechanism of enhancement in the sensing performance of nCOPA with respect to NH₃ was also discussed in detail. This work aims to improve the NH₃ sensing performance by modifying the chemical structure. This is achieved by reducing the imine (C=N) linkage covalent organic polymer to amine (C-N) linkage covalent organic polymer.

4.2 Aims and Objectives

The aims and objectives of the current work are mentioned as follows:

- To synthesize an imine-linkage nanoporous covalent organic polymer (nCOPI), further, nCOPI to be reduced to aminelinkage nCOP (nCOPA).
- (ii) To investigate the presence of imine and amine linkage in nCOPI and nCOPA, respectively through FT-IR and ¹³C CP-MAS NMR.
- (iii) To evaluate the thermal stability and surface morphology of the nCOPI and nCOPA.
- (iv) To investigate the sensing performance of nCOPI and nCOPA for detecting NH_3 at RT.
- To investigate the selectivity, dynamic response at different concentrations, and effect of humidity on sensing response of nCOPA to NH₃.

 (vi) To investigate the proposed sensing mechanism of the nCOPA sensor towards NH₃.

4.3 Experiemental Section

4.3.1 Chemical and Methods

The chemicals and reagents were bought commercially and utilized without purification. 4-Formylphenylboronic acid was obtained from SRL, India and bis(triphenylphosphine)palladium (II) dichloride (Pd(PPh₃)₂Cl₂) was bought from TCI. 3,4-Diaminobenzhydrazide, sodium borohydride (NaBH₄) and potassium carbonate (K₂CO₃) were purchased from Sigma Aldrich. 1,3,5-Tribromobenzene was purchased from Alfa Aesar. All the solvents used in the reaction were purchased from Merck and purified using the standard method before use. The progress of the reaction was monitored by thin-layer chromatography (TLC, aluminium plates covered with silica gel 60 F254). The intermediate was purified by flash column chromatography using 100-200 mesh size silica gel.

4.3.2 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1''-terphenyl]-4,4''dicarbaldehyde (TP3F), Imine Linkage Nanoporous Covalent Organic Polymer (nCOPI) and Amine Linkage Nanoporous Covalent Organic Polymer (nCOPA)

Scheme 4.1 Synthetic scheme for solution phase synthesis 5'-(4formylphenyl)-[1,1':3',1"-terphenyl]-4,4"-dicarbaldehyde (TP3F), Imine Linkage Nanoporous Covalent Organic Polymer (nCOPI) and Amine Linkage Nanoporous Covalent Organic Polymer (nCOPA)



4.3.2.1 Synthesis of 5'-(4-formylphenyl)-[1,1':3',1''-terphenyl]-4,4''dicarbaldehyde (TP3F, 3)

500 mg of 1,3,5-tribromobenzene (1, 1.59 mmol) and 1.07 g of 4formlyphenylboronic acid (2, 7.13 mmol) were dissolved in toluene (15 mL) and H₂O (5 mL). The above reaction mixture was purged with nitrogen for 30 min and then, 1.05 g potassium carbonate (7.6 mmol) was added to the above mixture followed by the addition of 44.6 mg of Pd(PPh₃)₂Cl₂ (4 mol%). The reaction was refluxed at 90 °C and stirred under an inert atmosphere for 48 h. The solvent was evaporated under reduced pressure. The product was dissolved in DCM and passed through celite. The product was extracted using DCM and washed with deionized water (3 \times 30 mL). The DCM layer was dried over Na₂SO₄ and the solvent was evaporated under reduced pressure to obtain a solid compound. The crude compound was purified using flash chromatography using silica gel (100-200 mesh) eluted with EtOAc: hexane (3:7) as a mobile phase to obtain a desired pale brown product (Scheme 4.1). Yield: 74% (460 mg, 1.18 mmol).

¹H NMR (CDCl₃, 500 MHz): 10.11 (s, 3H, H of CHO), 8.04-8.02 (d, 6H, Ph ring, J = 8.25 Hz), 7.91 (s, 3H, H of Ph ring), 7.89-7.87 (d, 6H, Ph ring, J = 8.2 Hz). ¹³C NMR (CDCl₃, 125 MHz): $\delta = 191.78$, 146.3, 141.6, 135.76, 130.46, 127.99 and 126.49.



- 10.11





Figure 4.1 ¹H NMR spectrum (500 MHz, CDCl₃) of TP3F (3).



Figure 4.2 ¹³C NMR spectrum (125 MHz, CDCl₃) of TP3F (3).

4.3.2.2 Synthesis of Imine Linkage Nanoporous Covalent Organic Polymer (nCOPI)

The nCOPI was synthesized using the same procedure that has already been reported [32]. 3,4-Diaminobenzhydrazide (62 mg, 0.12 mmol) and TP3F (100 mg, 0.12 mmol) were dissolved in 40 mL methanol and 6 M acetic acid. The mixture was then refluxed for 3 days at 90 °C. After 3 days, the product was filtered, washed with water and ethanol, and dried at 60 °C for 8 h in the oven to obtain the yellow product (**Scheme 4.1**). The yellow product, named nCOPI, was characterized by FT-IR.

4.3.2.3 Synthesis of Amine Linkage Nanoporous Covalent Organic Polymer (nCOPA)

The imine bond of nCOPI was reduced to amine bonds using a previously reported procedure [33]. To do this, 100 mg nCOPI and 25 mg NaBH₄ were dispersed in a flask with 30 mL of methanol. The reaction mixture was refluxed for 7 days. After the completion of the reaction, the product was filtered, washed with water and ethanol. The obtained product, named nCOPA, was then dried at 60 $^{\circ}$ C in an oven for

7 h to remove any entrapped water and ethanol to obtain a yellow solid (**Figure 4.3a**).

4.3.3 Characterization Techniques

A powder X-ray diffractometer was used to observe the X-ray diffraction patterns (XRD) of the materials (Empyrean, Malvern Panalytical X-ray diffractometer) in the 20 region of 5–60° with Cu-Ka radiation (λ = 1.54 Å). To explore the surface morphology of the materials scanning electron microscopy (SEM: Supra55 Zeiss) with energy dispersive Xrays (EDS) and high-resolution transmission electron microscopy (HRTEM: Field Emission Gun-Transmission Electron Microscope 300 kV, model no Tecnai G2, F30) was performed. X-ray photoelectron spectroscopy (XPS: Thermoscientific NEXA Surface analyzer) was used to analyze the composition of the polymers. Fourier transform infrared (FT-IR) spectroscopy of monomers and polymers was observed on Bruker (Tensor-27) in the range 600 to 3700 cm⁻¹. The Brunauer-Emmett-Teller (BET) surface area and pore size of monomer and polymer were calculated using quantachrome, Autosorb iQ2. Thermogravimetric (TGA: Mettler Toledo Thermal Analyzer) analysis was performed with constant heat of 10 °C/min in the range of 27 to 800 °C under a nitrogen atmosphere. ¹³C Cross Polarization Magic Angle Spinning Nuclear Magnetic Resonance (¹³C CP-MAS NMR) was observed on 500 MHz Bruker Advance Neo NMR. ¹H and ¹³C NMR of the compound were observed on Bruker AV 500 MHz instrument using the chloroform-d (CDCl₃) as a solvent and TMSA was used as an internal standard.

4.3.4 H₂S Sensor Fabrication and Characterization

4.3.4.1 Device fabrication: nCOPA powder was mixed with water, ethanol, and 10 μ L nafion (binder) to make a thick paste. This paste was then dropcasted onto a platinum interdigitated electrode (IDE). The fabricated device was heated in an oven at 80 °C for 24 h to enhance the stability of the nCOPA. The same procedure was repeated for fabricating

nCOPI. The response of both sensors is determined by the changes in resistance (Figure 4.3b).



Figure 4.3 (a) Synthetic scheme of conversion of imine-based nCOP to amine-based nCOP and (b) schematic illustration of fabrication of nCOP on IDE.

4.3.4.2 Sensing setup and measurements: The sensing experiment was performed in the dynamic flow-through measurement system, which includes a stainless steel chamber with an internal volume of approximately 500 cm³. The sensor's contact pads were connected to the Keithley 2612A source meter, which was used to observe the change in the resistance during exposure or removal of the targeted gas with a constant bias voltage of 10 mV. The flow rate of the NH₃ was controlled by a mass flow controller, MFC (model: Alicat®, MC 1slpm, USA). The detailed illustration of it is presented is included in the Supporting Information under H₂S sensor fabrication and measurement and also described elsewhere [34]. The response of nCOPI and nCOPA sensors was calculated using the following equation (1):

$$Response\% (R) = \frac{R_g - R_a}{R_a} \times 100$$
(4.1)

where, R_g and R_a represent the resistance of the fabricated device in the presence of targeted analyte and air, respectively. The response/recovery

time is calculated as the time it takes for the resistance to change by 90% after being exposed to the targeted gas/air [35]. All the sensing experiments were carried out at atmospheric humidity and room temperature. Different concentrations of NH₃ were measured by mixing synthetic air with NH₃ gas molecules and the flow rate was controlled using a mass flow controller (MFC). The high purity (99.9%) cylinders of SO₂, H₂S, NH₃, CO₂, CO, and NO₂ gases were commercially purchased from air gas material of known concentration and used to achieve different gaseous environments in the chamber for selectivity experiment. The sensing performance of NH₃ was investigated under different relative humidity (RH) levels, which were achieved by using saturated solutions of Mg(NO₃)₂, NaCl, and K₂SO₄ to obtain 57, 75, and 97% RH, respectively [36]. The LOD and LOQ are calculated as follows:

$$LOD = \frac{3 \times SD}{\sigma} \tag{4.2}$$

$$LOQ = \frac{10 \times SD}{\sigma} \tag{4.3}$$

where, *SD* represents the standard deviation of the response of the calibrated curve and σ represents the slope of the calibrated curve.

4.4 Results and Discussion

Fourier-transform infrared (FT-IR) analysis was performed to confirm the presence of functional groups in 3,4-diaminobenzhydrazide, TP3F, nCOPI, and nCOPA (**Figure 4.4a**). The FT-IR spectra of 3,4diaminobenzhydrazide exhibit significant peaks at 3393, 1623, and 1575 cm⁻¹, corresponding to NH₂, C=O (amide I), and C–N (amide II), respectively [37,38]. In TP3F, the peak observed at 1680 cm⁻¹ is attributed to C=O [39,40]. In nCOPI, the appearance of a peak at 1601 cm⁻¹ and the disappearance of the peak at 1680 cm⁻¹ confirm the formation of a C=N functional group [41]. Additionally, the appearance of peaks at 3345 (stretching frequency of NH), 1595 (bending stretch of C-N-H bond), 1355 (stretching frequency of C–N), and 1212 cm⁻¹ (vibration stretching of C–N bond in the secondary amine linkage) in the nCOPA spectra confirms the presence of C–N bonds [37,42]. Furthermore, a powder X-ray diffraction (PXRD) experiment was performed to analyze the amorphous and crystalline properties of TP3F, nCOPI, and nCOPA (**Figure 4.4b**). The PXRD spectra of 3,4-diaminobenzhydrazide and TP3F show sharp peaks, indicating their crystalline behavior, while nCOPI and nCOPA exhibit sharp peaks with a slightly broad hump, indicating their lower degree of crystallinity [17,39,43].



Figure 4.4 (a) FT-IR spectra of 3,4-diaminobenzhydrazide, TP3F, nCOPI, and nCOPA. (b) PXRD spectrum of 3,4-diaminobenzhydrazide, TP3F, nCOPI, and nCOPA. (c) ¹³C CP-MAS NMR spectrum of nCOPA.

Furthermore, the formation of nCOPA was confirmed using ¹³C CP-MAS NMR. In the solid-state ¹³C CP-MAS NMR of nCOPA, peaks were observed at $\delta = 166.16$, 140.43, 133.92, 127.05, and 30.6 ppm, which correspond to C=O, sp²-hybridized carbons, and aliphatic CH₂ (**Figure 4.4c**) [44,45,46]. Moreover, there was no peak detected around 158 ppm, suggesting that the imine linkage was not present [47]. Instead, a small peak at 45.58 ppm was observed, which is attributed to the amine (C–N) bond. Thus, the absence of a peak around 158 ppm and the appearance of peaks at 45.58 and 30.6 ppm confirm the absence of an imine bond and the presence of amine (C–N) linkage in the nCOPA, respectively [33,42]. Therefore, the results obtained from ¹³C CP-MAS NMR confirm the successful formation of the amine bond in nCOPA. These results were also supported by FT-IR analysis.



Figure 4.5 FE-SEM images of as-synthesized (a) TP3F, (b) nCOPI and (c) nCOPA. (d)-(i) EDS pattern and elemental mapping of nCOPI. (h)-(k) EDS pattern and elemental mapping of nCOPA. HR-TEM images of (l) nCOPI and (m) nCOPA.

The surface morphology of nCOPI, nCOPA, and TP3F was analyzed using field emission scanning microscopy (FE-SEM) (**Figure 4.5a-4.5c**). The TP3F displays a smooth surface with rodlike morphology [48], while nCOPI shows rough nanospheres [49] and nCOPA shows nanorod-like morphology [50], which are randomly distributed on the surface. Energy-dispersive X-ray spectroscopy (EDS) pattern and elemental

mapping of nCOPI and nCOPA confirm the presence of C, N, and O and a homogenous distribution of C, N, and O over the entire surface, respectively (**Figure 4.5d-4.5k**). To validate the SEM images, highresolution transmission electron microscopy (HR-TEM) was performed, confirming the nanosphere-like morphology of nCOPI and nanorod-like morphology of nCOPA (**Figure 4.5l and 4.5m**).



Figure 4.6 Nitrogen sorption isotherm of (a) TP3F, (b) nCOPI, and (c) nCOPA. (d) Thermal stability curve of TP3F, nCOPI, and nCOPA.

The surface area and porosity of TP3F, nCOPI, and nCOPA were evaluated by performing N₂ adsorption/desorption analysis at 77 K (**Figure 4.6a-4.6c**). The Brunauer–Emmett–Teller (BET) surface area was calculated to be 10.8, 14.4, and 21.23 m²/g for TP3F, nCOPI, and nCOPA, respectively. The surface values clearly show that nCOPA has a larger BET surface area compared to TP3F and nCOPI. Furthermore, the thermal stability of TP3F, nCOPI, and nCOPA is observed using a thermogravimetric experiment in an N₂ environment (**Figure 4.6d**). The results of the thermogravimetric (TGA) curve show that TP3F, nCOPI, and nCOPA exhibit small weight loss before 215, 290, and 350 °C, respectively, due to adsorbed water molecules and guest solvents.⁵¹
Moreover, TP3F, nCOPI, and nCOPA display continuous weight loss within the temperature ranges of 215–520, 290–598, and 350–646 °C, respectively. This demonstrates the degradation of TP3F, nCOPI, and nCOPA within these temperature range [44].



Figure 4.7 (a) XPS survey spectrum of nCOPI. Deconvoluted spectra of (b) C1s (c) N1s and (d) O1s of nCOPI. (e) XPS survey spectrum of nCOPA. Deconvoluted spectra of (f) C1s, (g) N1s and (h) O1s of nCOPA.

The surface composition and valence of the elements in nCOPI and nCOPA were investigated using the X-ray photoelectron (XPS) experiment. The survey spectra of nCOPI and nCOPA reveal the presence of elements C, N, and O (Figures 4.7a and 4.7e). The deconvoluted C1s spectrum of nCOPI displays four peaks at binding energies of 284.2, 285.1, 286., and 288.1 eV, ascribing to C=C, C-N, C=N, and C=O, respectively (Figure 4.7b) [40,52]. After the reduction of imine (C=N) to amine (C-N), the C1s spectrum exhibits three peaks at binding energies of 284.2, 285.4, and 288.5 eV, corresponding to C=C, C-N, and C=O, respectively (Figure 4.7f) [40,52]. The deconvoluted N 1s spectrum of nCOPI exhibits three peaks at 398.7, 399.9, and 401.3 eV, indicating C=N, C-N, and N-C=O, respectively (Figure 4.7c) [40,53]. After the reduction of imine (C=N) to amine (C-N), the deconvoluted N1s spectrum of nCOPA shows three peaks at binding energies of 399.2, 399.9, and 400.4 eV, ascribing to -NH, C-N, and N-C=O, respectively (Figure 4.7g). The deconvoluted O 1s spectra of nCOPI and nCOPA exhibit one peak at 532.4 eV, attributed to C=O (Figure 4.7d and 4.7h) [40,54].

4.4.1 NH₃ Sensing Performance

The current-voltage (*I-V*) analysis was performed at a constant voltage range of -5 to 5 V to study the charge-transport activity at a temperature of 25 °C (**Figure 4.8a**). The *I-V* curve demonstrates linear behavior, indicating an ohmic nature of the nCOPA sensor [9,35]. The current is observed in nanoamperes, indicating that it is a low-power device.

The sensing performance of nCOPI and nCOPA was investigated by exposing them to 500 ppm of NH₃ at 25 °C. When NH₃ gas molecules came into contact with the surface of nCOPI and nCOPA sensors, a gradual increase in resistance of the sensing material was observed, indicating that they are of p-type nature [55]. **Figure 4.8b**, clearly depicts that nCOPA exhibits a significantly higher response, 18.8 folds higher compared to nCOPI. The nCOPA sensor shows a response of 91% to 500 ppm of

NH₃, with a response/recovery time of 60/70 s. **Figure 4.8c** displays the transient response curve of the nCOPA sensor to NH₃ at 25 °C. The sensing performance of the nCOPA sensor to 100 ppm of NO₂, H₂S, CO₂, NH₃, SO₂, and CO gases was studied and compared at 25 °C. The response values of the nCOPA sensor to NO₂, H₂S, CO₂, NH₃, SO₂, and CO gases was studied and compared at 25 °C. The response values of the nCOPA sensor to NO₂, H₂S, CO₂, NH₃, SO₂, and CO are 50, 79.9, 100, 640, 110, and 54%, respectively (**Figure 4.8d**). The selectivity coefficients of the nCOPA sensor (K = R_{NH3}/R_{other analyte}) are calculated to be greater than 5.8, indicating its excellent selectivity to NH₃.



Figure 4.8 (a) Current-voltage (*I-V*) curve of nCOPA fabricated sensor at 25 °C. (b) Comparison of response for nCOPI and nCOPA towards 500 ppm NH₃ at 25 °C. (c) Single cycle response curve of nCOPA with response/recovery time towards 500 ppm NH₃. (d) Response of nCOPA towards different gases at 100 ppm at 25 °C. (e) Dynamic response curve of nCOPA from 1 to 500 ppm NH₃ concentration at 25 °C and (f)

response of nCOPA towards 500 ppm NH_3 under different humid (57% to 97% RH) condition at 25 °C.

The dynamic response/recovery curve of the chemiresistive nCOPA sensor was evaluated for concentrations of NH₃ ranging from 1 to 500 ppm at a temperature of 25 °C (**Figure 4.8e**). The responses of the nCOPA sensor are observed to be 116, 205, 293, 459, 640, 1010, and 1700% for concentrations of 1, 10, 25, 50, 100, 250 and 500 ppm, respectively. The response value was found to be excellent even at low concentrations, specifically at the threshold limit value (TLV) of 25 ppm set by OSHA [56]. The significant increase in sensing performance with concentration is dependent on the number of NH₃ molecules that are adsorbed and desorbed on the surface of the sensing layer. On the contrary, when the synthetic was exposed to the sensing chamber, the resistance of nCOPA returned to its baseline resistance and showed excellent reversible behavior at all concentrations.

The performance of the nCOPA sensor in detecting 500 ppm NH₃ was also investigated under different relative humidity (RH) conditions at 25 °C (**Figure 4.8f**). The response of the nCOPA sensor to NH₃ was found to be 1430, 1350, and 1290% under RH conditions of 57, 75, and 97%, respectively. It is clear that the response decreases as the RH increases. This could be due to that water molecules compete with NH₃ molecules to occupy the active sites of the nCOPA sensor, which limits the number of active sites available for the adsorption of NH₃ gas molecules on the surface of the nCOPA sensor. As a result, the response of the nCOPA sensor to NH₃ decreases under high RH [34]. However, even at higher RH (97%), the nCOPA sensor still exhibits an excellent response of 1290%, indicating its suitability for use in high humidity conditions. The correlation between the concentration of NH₃ and the response values of nCOPA displays remarkable linearity, with LOD and LOQ values of 0.25 ppb and 0.86 ppb, respectively (**Figure 4.9a**).



Figure 4.9 (a) Correlation between response of nCOPA and different concentrations of NH_3 (b) Repeatability assessment of nCOPA sensor towards 500 ppm NH_3 for 5 consecutive cycles at 25 °C. (c) Long-term stability curve of nCOPA at every 5th day for 60 days at 25 °C and (d) response of nCOPA to 500 ppm NH_3 at different temperatures.

The repeatability behaviour of nCOPA sensor was studied by exposing it to 500 ppm NH₃ gas for five consecutive cycles (**Figure 4.9b**). The nCOPA sensor displays excellent repeatability and reversibility after each cycle, with minimal drift in its response to NH₃ gas. Subsequently, a stability test was conducted on the nCOPA sensor's response to 500 ppm NH₃ every 5th day for a period of 2 months (**Figure 4.9c**). The response values did not fluctuate significantly, indicating excellent longterm stability of the nCOPA sensor. Further, the response of the nCOPA sensor to NH₃ at different temperatures (50, 100, 150, and 200 °C) was observed. It is noted that as the operating temperature increased, the nCOPA sensor's response to NH₃ decreased (**Figure 4.9d**). Interestingly, The nCOPA sensor exhibits a maxium response at 25 °C. The possible reason for low sensing at higher temperatures could be that the increased molecular vibrations in the nCOPA hinder the interactions between NH₃ molecules and nCOPA [32]. Another possible reason could be that at higher temperatures, the equilibrium between adsorption and desorption shifts towards desorption, leading to a reduced response of nCOPA to NH_3 [57,58].

4.4.2 Sensing Mechanism

The gas sensing mechanism could be attributed to the charge transfer and surface reactions between the sensing material and gas molecules. Specifically, gas molecules interact with sensing material to facilitate the physical adsorption of gas molecules with the surrounding charge carriers [59].

When NH₃ was exposed to the chamber and came into contact with the surface of the nCOPA sensor, a significant increase in the resistance was observed. This increase in resistance could be attributed to the charge transfer effect from NH₃ molecules, which act as electron donors, to the electron-deficient p-type nCOPA, where the predominant carriers are holes. Once the NH₃ molecules are adsorbed on the active sites of the nCOPA surface, they inject electrons into the holes of nCOPA. The electrons injected by NH₃ molecules interact with the majority of holes in nCOPA, leading to a reduction in the number of charge carriers (holes) in the sensing material (nCOPA). This decrease in carrier density leads to an increase in the resistance of nCOPA. The resistance stabilizes when the number of NH₃ molecules adsorbed on the nCOPA surface reaches its saturation level, as there are no vacant adsorption sites available (Scheme 4.2a). The NH₃ molecules gradually desorbed from the nCOPA adsorption site when the sensing material is exposed to synthetic air. After the desorption of NH₃ molecules, the resistance of the nCOPA sensor decreases and slowly returns to its initial value. Moreover, a higher surface area accelerates the desorption process of NH₃ gas molecules, leading to complete reversibility of the sensors at 25 °C. Therefore, nCOPA sensors are completely reversible and do not require any additional steps like thermal annealing, vacuum, or degassing vacuum, etc to restore its parameters [52,60,61,62,63].

Scheme 4.2 (a) Schematic representation of sensing mechanism based on electron transfer between the NH_3 (act as electron donor) and p-type nCOPA (electron acceptor, where the majority carriers are holes) and (b) hydrogen bonding between NH_3 gas molecules and nCOPA sensor



Another possible reason for the high selectivity of the nCOPA sensor to NH₃ could be due to non-covalent interaction. In an NH₃ environment, NH₃ molecules can interact with amine (–NH) functional groups of the nCOPA via hydrogen bonding (**Scheme 4.2b**) [17,32,52,64,65]. This interaction subsequently weakens the conjugation in the backbone of the nCOPA, resulting in a decrease in the mobility of charge carriers (holes) [66]. As a result, a significant increase in the resistance was observed in the nCOPA sensor, and the corresponding response value of nCOPA to NH₃ was calculated. Therefore, the nCOPA sensor can be used to selectively detect NH₃ at 25 °C, which is useful for monitoring and protecting the environmental pollution and human health risks. However, understanding the accurate sensing mechanism of imine and amine-containing polymers will be an important area of research in the future.

The response of the nCOPA sensor to NH_3 was compared with other studies in the literature. Various sensing parameters such as response, concentration, and response/recovery time are compared to previously published reports that were conducted at 25 °C (**Table 4.1**).

Table 4.1 Comparison of room temperature response of nCOPA sensor

 towards NH₃ with other reported literature

S.	Materials	Concentra	Respo	Response/rec	Refere
Ν		tion	nse	overy time (s)	nce
0.		(ppm)	(%)		
1.	MXene/TiO ₂ /C-	100	6.84%	76/62 s	67
	NFs				
2.	pCTF	100	-35%	54/200 s	68
3.	CTF-1-A	100	-17.2%	100/420 s	69
4.	rGO-CuFe ₂ O ₄	200	24.4%	3/6 s	70
5.	CuTSPc@3D-	1000	91%	138/63 s	71
	(N)GF/PEDOT-				
	PSS				
6.	SWCNT-	50	102%	2.7/7.7 min	72
	SO ₃ H/PEDOT				
7.	MoS ₂ /Mo ₃	50	55%	45/53 s	73
8.	PEDOT:PSS/M	1000	95%	116/40 s	74
	Xene				
9.	Graphene/PEDO	500	9.6%	180 s	75
	T:PSS				
10	Cu-3-PMN-20	100	17.11	41/179 s	61
•					
11	PCN	200	19.53	134/624 s	60
•					
12	nCOPA	100	640	60/70 s	This

•					work		

4.5 Conclusion

In summary, nCOPI was successfully synthesized and imine bonds in nCOPI were reduced to form a polymer based on the amine group, which was named nCOPA. Both nCOPI and nCOPA were comprehensively characterized using various techniques. The presence of functional groups and the successful formation of nCOPI and nCOPA were confirmed through FT-IR and ¹³C CP-MAS NMR analysis. nCOPI and nCOPA were then fabricated on an IDE for detecting NH₃ gas under ambient conditions. The sensing result demonstrates that nCOPA exhibited a significantly higher response, with an increase of 18.8 times reaching 1700%, compared to nCOPI, which showed a response of 90%. The response/recovery time for nCOPA was 60/70 s. This demonstrated that the reduction of imine to amine in nCOPA significantly improved its sensing performance to detect NH₃. The response of the nCOPA sensor to NH₃ was observed at concentrations ranging from 1 to 500 ppm, with LOD and LOQ values of 0.25 and 0.86 ppb, respectively. Additionally, the sensing performance of nCOPA was investigated under different levels of RH and consistently showed an excellent response to NH₃. Moreover, the nCOPA sensor showed excellent selectivity, repeatability, reversibility, and long-term stability. These findings highlight the potential of nCOPA as a promising sensing candidate for detecting NH₃ under normal environmental conditions. The excellent response of nCOPA could be attributed to the charge transfer and hydrogen bonding between NH₃ gas molecules and nCOPA.

4.6 References

 Sun N., Tian Q., Bian W., Wang X., Dou H., Li C., Zhang Y., Gong C., You X., Du X., Yin P., Zhao X., Yang Y., Liu X., Jing Q., Liu B. (2023), Highly Sensitive and Lower Detection-Limit NO₂ Gas Sensor Based on Rh-Doped ZnO Nanofibers Prepared by Electrospinning, Appl. Surf. Sci., 614, 156213 (DOI: 10.1016/j.apsusc.2022.156213).

- (2) Shi Z., Zhang J., Zeng W., Zhou Q. (2023), Adsorption and Sensing Performances of MoTe₂ Monolayers Doped with Pd, Ni, and Pt for SO₂ and NH₃: A DFT Investigation, Langmuir, 39, 4125-4139 (DOI: 10.1021/acs.langmuir.3c00030).
- (3) Bhati V. S., Kumar M., Banerjee R. (2021), Gas Sensing Performance of 2D Nanomaterials/Metal Oxide Nanocomposites: A Review, J. Mater. Chem. C, 9, 8776–8808 (DOI: 10.1039/d1tc01857d).
- McEnaney J. M., Singh A. R., Schwalbe J. A., Kibsgaard J., Lin J. C., Cargnello M., Jaramillo T. F., Nørskov J. K. (2017), Ammonia Synthesis from N₂ and H₂O Using a Lithium Cycling Electrification Strategy at Atmospheric Pressure, Energy Environ. Sci., 10, 1621–1630 (DOI: 10.1039/c7ee01126a).
- (5) Tian X., Cui X., Xiao Y., Chen T., Xiao X., Wang Y. (2022), Pt/MoS₂/Polyaniline Nanocomposite as a Highly Effective Room Temperature Flexible Gas Sensor for Ammonia Detection, ACS Appl. Mater. Interfaces, 15, 9604-9617 (DOI: 10.1021/acsami.2c20299).
- (6) Timmer B., Olthuis W., Van Den Berg A. (2005), Ammonia Sensors and Their Applications-A Review, Sensors Actuators, B Chem., 107, 666–677 (DOI: 10.1016/j.snb.2004.11.054).
- Davies S., Spanel P., Smith D. (1997), Quantitative Analysis of Ammonia on the Breath of Patients in End-Stage Renal Failure, Kidney Int., 52, 223–228 (DOI: 10.1038/ki.1997.324).
- (8) Liu C., Duan Z., Zhang B., Zhao Y., Yuan Z., Zhang Y., Wu Y., Jiang Y., Tai H. (2023), Local Gaussian Process Regression with Small Sample Data for Temperature and Humidity Compensation of Polyaniline-Cerium Dioxide NH₃ Sensor, Sensors Actuators B Chem., 378, 133113 (DOI: 10.1016/j.snb.2022.133113).
- (9) He T., Sun S., Huang B., Li X. (2023), MXene/SnS₂ Heterojunction for Detecting Sub-Ppm NH₃ at Room Temperature, ACS Appl. Mater. Interfaces, 15, 4194–4207 (DOI: 10.1021/acsami.2c18097).
- (10) Alagh A., Annanouch F. E., Sierra-Castillo A., Haye E., Colomer

J. F., Llobet E. (2022), Three-Dimensional Assemblies of Edge-Enriched WSe₂ Nanoflowers for Selectively Detecting Ammonia or Nitrogen Dioxide, ACS Appl. Mater. Interfaces, 14, 54946– 54960 (DOI: 10.1021/acsami.2c16299).

- (11) Manoharan M., Govindharaj K., Muthumalai K., Pandian R., Haldorai Y., Rajendra Kumar R. T. (2023), Highly Selective Room Temperature Detection of NH_3 and NO_x Using Oxygen-Deficient $W_{18}O_{49}$ -Supported WS_2 Heterojunctions, ACS Appl. Mater. Interfaces, 15, 4703–4712 (DOI: 10.1021/acsami.2c18732).
- (12) Li M., Tang J., Luo Y., Yang J., Liu J., Peng J., Fang Y. (2022), Imine Bond-Based Fluorescent Nanofilms toward High-Performance Detection and Efficient Removal of HCl and NH₃, Anal. Chem., 95, 2094-2010 (DOI: 10.1021/acs.analchem.2c05059).
- (13) Bai S., Yin P., Zhao Y., Tang P., Luo R., Li D., Chen A. (2023), RGO-Modified ZnWO₄/WO₃ Nanocomposite for Detection of NH₃, J. Phys. Chem. C, 127, 9315-9326 (DOI: 10.1021/acs.jpcc.3c00718).
- (14) Lu Q., Huang L., Hao X., Li W., Wang B., Wang T., Liang X., Liu F., Wang C., Lu G. (2021), Mixed Potential Type NH₃ Sensor Based on YSZ Solid Electrolyte and Metal Oxides (NiO, SnO₂, WO₃) Modified FeVO₄ Sensing Electrodes, Sensors Actuators, B Chem., 343, 130043 (DOI: 10.1016/j.snb.2021.130043).
- Wang Q., Wang A., Dou Y., Shen X., Sudi M. S., Zhao L., Zhu W., Li L. (2022), A Tin Porphyrin Axially-Coordinated Two-Dimensional Covalent Organic Polymer for Efficient Hydrogen Evolution, Chem. Commun., 58, 7423–7426 (DOI: 10.1039/d2cc02775e).
- (16) Yadav D.; Subodh N.; Awasthi S. K. (2022), Recent Advances in the Design, Synthesis and Catalytic Applications of Triazine-Based Covalent Organic Polymers, Mater. Chem. Front., 6, 1574– 1605, DOI: 10.1039/d2qm00071g.
- (17) Sharma M., Patel C., Sriram S., Mukherjee S., Das A. K. (2023),

Investigating the Role of Amide to Thioamide Substitution of a Covalent Organic Polymer for the Selective Chemodetection of H_2S at Room Temperature, ACS Appl. Polym. Mater., 5, 10065-10072 (DOI: 10.1021/acsapm.3c01872).

- (18) Liu X., Zheng W., Kumar R., Kumar M., Zhang J. (2022), Conducting Polymer-Based Nanostructures for Gas Sensors, Coord. Chem. Rev., 462, 214517 (DOI: 10.1016/j.ccr.2022.2145 17).
- (19) Chung J., Khot A., Savoie B. M., Boudouris B. W. (2020), 100th Anniversary of Macromolecular Science Viewpoint: Recent Advances and Opportunities for Mixed Ion and Charge Conducting Polymers, ACS Macro Lett., 9, 646–655 (DOI: 10.1021/acsmacrolett.0c00037).
- (20) Ravi S., Kim J., Choi Y., Han H. H., Wu S., Xiao R., Bae Y. S. (2023), Metal-Free Amine-Anchored Triazine-Based Covalent Organic Polymers for Selective CO₂ Adsorption and Conversion to Cyclic Carbonates Under Mild Conditions, ACS Sustain. Chem. Eng., 11, 1190–1199 (DOI: 10.1021/acssuschemeng.2c06621).
- (21) Han X. H., Liang R. R., Zhou Z. B., Qi Q. Y., Zhao X. (2023), Converting an Amorphous Covalent Organic Polymer to a Crystalline Covalent Organic Framework Mediated by a Repairing Agent, Chem. Commun., 59, 2461–2464 (DOI: 10.1039/d2cc05800f).
- (22) Skorjanc T., Shetty D., Valant M. (2021), Covalent Organic Polymers and Frameworks for Fluorescence-Based Sensors, ACS Sensors, 6, 1461–1481 (DOI: 10.1021/acssensors.1c00183).
- (23) Roy Chowdhury A., Maiti S., Mondal A., Das A. K. (2020), Picolinohydrazide-Based Covalent Organic Polymer for Metal-Free Catalysis and Removal of Heavy Metals from Wastewater, J. Phys. Chem. C, 124, 7835–7843 (DOI: 10.1021/acs.jpcc.0c00664).
- Niu F., Shao Z. W., Zhu J. L., Tao L. M., Ding Y. (2021), Structural Evolution of Imine-Linked Covalent Organic Frameworks and Their NH₃ Sensing Performance, J. Mater.

Chem. C, 9, 8562-8569 (DOI: 10.1039/d1tc01662h).

- (25) Xu N., Wang R. L., Li D. P., Zhou Z. Y., Zhang T., Xie Y. Z., Su Z. M. (2018), Continuous Detection of HCl and NH₃ Gases with a High-Performance Fluorescent Polymer Sensor, New J. Chem., 42, 13367–13374 (DOI: 10.1039/c8nj02344a).
- (26) Ravi S., Puthiaraj P., Yu K., Ahn W. S. (2019), Porous Covalent Organic Polymers Comprising a Phosphite Skeleton for Aqueous Nd(III) Capture, ACS Appl. Mater. Interfaces, 11, 11488–11497 (DOI: 10.1021/acsami.9b00546).
- (27) Krounbi L., Enders A., Anderton C. R., Engelhard M. H., Hestrin R., Torres-Rojas D., Dynes J. J., Lehmann J. (2020), Sequential Ammonia and Carbon Dioxide Adsorption on Pyrolyzed Biomass to Recover Waste Stream Nutrients, ACS Sustain. Chem. Eng., 8, 7121–7131, DOI: 10.1021/acssuschemeng.0c01427.
- (28) Belowich M. E., Stoddart J. F. (2012), Dynamic Imine Chemistry, Chem. Soc. Rev., 41, 2003–2024 (DOI: 10.1039/c2cs15305j).
- (29) Halder A., Karak S., Addicoat M., Bera S., Chakraborty A., Kunjattu S. H., Pachfule P., Heine T., Banerjee R. (2018), Ultrastable Imine-Based Covalent Organic Frameworks for Sulfuric Acid Recovery: An Effect of Interlayer Hydrogen Bonding, Angew. Chemie - Int. Ed., 57, 5797–5802 (DOI: 10.1002/anie.201802220).
- (30) He Y., Xu T., Hu J., Peng C., Yang Q., Wang H., Liu H. (2017), Amine Functionalized 3D Porous Organic Polymer as an Effective Adsorbent for Removing Organic Dyes and Solvents, RSC Adv. 7, 30500–30505 (DOI: 10.1039/c7ra04649a).
- (31) Nketia-Yawson B., Jung A. R., Noh Y., Ryu G. S., Tabi G. D., Lee K. K., Kim B., Noh Y. Y. (2017), Highly Sensitive Flexible NH₃ Sensors Based on Printed Organic Transistors with Fluorinated Conjugated Polymers, ACS Appl. Mater. Interfaces, 9, 7322–7330 (DOI: 10.1021/acsami.6b14220).
- (32) Maiti S., Mandal B., Sharma M., Mukherjee S., Das A. K. (2020),A Covalent Organic Polymer as an Efficient Chemosensor for Highly Selective H₂S Detection through Proton Conduction,

Chem. Commun., 56, 9348–9351 (DOI: 10.1039/d0cc02704a).

- (33) Zhang M., Li Y., Yuan W., Guo X., Bai C., Zou Y., Long H., Qi Y., Li S., Tao G., Xia C., Ma L. (2021), Construction of Flexible Amine-Linked Covalent Organic Frameworks by Catalysis and Reduction of Formic Acid via the Eschweiler–Clarke Reaction, Angew. Chemie-Int. Ed., 60, 12396–12405 (DOI: 10.1002/anie. 202102373).
- (34) Patel C., Mandal B., Jadhav R. G., Ghosh T., Dubey M., Das A. K., Htay M. T., Atuchin V. V., Mukherjee S. (2022), S, N Co-Doped Carbon Dot-Functionalized WO₃ Nanostructures for NO₂ and H₂S Detection, ACS Appl. Nano Mater, 5, 2492–2500 (DOI: 10.1021/acsanm.1c04174).
- (35) Sharma M., Patel C., Maiti S., Mukherjee S., Das A. K. (2023), Fabricated Chemiresistive Sensor for Detection of Ethanol Using NDICY-ZnO Nanohybrid, IEEE Sens. J., 23, 15342–15349 (DOI: 10.1109/JSEN.2023.3276771).
- (36) Singh H., Tomer V. K., Jena N., Bala I., Sharma N., Nepak D., De Sarkar A., Kailasam K., Pal S. K. (2017), A Porous, Crystalline Truxene-Based Covalent Organic Framework and Its Application in Humidity Sensing, J. Mater. Chem. A, 5, 21820–21827 (DOI: 10.1039/c7ta05043g).
- (37) Coban Z. G., Yagci Y., Kiskan B. (2021), Catalyzing the Ring-Opening Polymerization of 1,3-Benzoxazines via Thioamide from Renewable Sources, ACS Appl. Polym. Mater., 3, 4203–4212 (DOI: 10.1021/acsapm.1c00637).
- (38) Schwaighofer A., Montemurro M., Freitag S., Kristament C., Culzoni M. J., Lendl B. (2018), Beyond Fourier Transform Infrared Spectroscopy: External Cavity Quantum Cascade Laser-Based Mid-Infrared Transmission Spectroscopy of Proteins in the Amide I and Amide II Region, Anal. Chem., 90, 7072–7079 (DOI: 10.1021/acs.analchem.8b01632).
- (39) Wang K., Yang H., Liao Z., Li S., Hambsch M., Fu G., Mannsfeld S. C. B., Sun Q., Zhang T. (2023), Monolayer-Assisted Surface-Initiated Schiff-Base-Mediated Aldol Polycondensation for the

Synthesis of Crystalline sp² Carbon-Conjugated Covalent Organic Framework Thin Films, J. Am. Chem. Soc., 145, 5203–5210 (DOI: 10.1021/jacs.2c12186).

- (40) Zhang S., Zhu K., Gao Y., Cao D. (2023), A Long Cycle Stability and High Rate Performance Organic Anode for Rechargeable Aqueous Ammonium-Ion Battery, ACS Energy Lett., 8, 889–897, DOI: 10.1021/acsenergylett.2c01962.
- (41) Liu S., Dou K., Liu B., Pang M., Ma P., Lin J. (2023), Construction of Multiform Hollow-Structured Covalent Organic Frameworks via a Facile and Universal Strategy for Enhanced Sonodynamic Cancer Therapy, Angew. Chemie Int. Ed., 62, e202301831 (DOI: 10.1002/anie.202301831).
- (42) Hu J., Zanca F., McManus G. J., Riha I. A., Nguyen H. G. T., Shirley W., Borcik C. G., Wylie B. J., Benamara M., Van Zee R. D., Moghadam P. Z., Beyzavi H. (2021), Catalyst-Enabled in Situ Linkage Reduction in Imine Covalent Organic Frameworks, ACS Appl. Mater. Interfaces, 13, 21740–21747 (DOI: 10.1021/acsami.1c02709).
- (43) Yang S., He P., Tian Y., Luo Y., Jiang J. (2023), In Situ Encapsulating Cobalt Phosphide into a Quasi-MOF: A High-Performance Catalyst for Hydrolytic Dehydrogenation of Ammonia Borane, New J. Chem., 47, 3151–3158 (DOI: 10.1039/d2nj05443d).
- (44) Yadav D., Awasthi S. K. (2019), An Unsymmetrical Covalent Organic Polymer for Catalytic Amide Synthesis, Dalt. Trans., 49, 179–186 (DOI: 10.1039/c9dt03931g).
- (45) Zhao G., Mei Z., Duan L., An Q., Yang Y., Zhang C., Tan X., Guo H. (2023), COF-Based Single Li⁺ Solid Electrolyte Accelerates the Ion Diffusion and Restrains Dendrite Growth in Quasi-Solid-State Organic Batteries, Carbon Energy, 5, e248 (DOI: 10.1002/cey2.248).
- (46) Lim J., Zhang S., Wang L., Seo D., Dickwella Widanage M. C., Pipe K. P., Ramamoorthy A., Kim J. (2023), Dihydroxy Indole-Free Poly(Catecholamine) for Smooth Surface Coating with

Amine Functionality, ACS Appl. Polym. Mater, 5, 6133–6142 (DOI: 10.1021/acsapm.3c00803).

- (47) Zhai Y., Liu G., Jin F., Zhang Y., Gong X., Miao Z., Li J., Zhang M., Cui Y., Zhang L., Liu Y., Zhang H., Zhao Y., Zeng Y. (2019), Construction of Covalent-Organic Frameworks (COFs) from Amorphous Covalent Organic Polymers via Linkage Replacement, Angew. Chemie Int. Ed., 58, 17679–17683 (DOI: 10.1002/anie.201911231).
- (48) Ma Y., Leng Y., Huo D., Zhao D., Zheng J., Yang H., Zhao P., Li F., Hou C. (2023), A Sensitive Enzyme-Free Electrochemical Sensor Based on a Rod-Shaped Bimetallic MOF Anchored on Graphene Oxide Nanosheets for Determination of Glucose in Huangshui, Anal. Method, 15, 2417–2426 (DOI: 10.1039/d2ay 01977a).
- (49) Sprachmann J., Wachsmuth T., Bhosale M., Burmeister D., Smales G. J., Schmidt M., Kochovski Z., Grabicki N., Wessling R., List-Kratochvil E. J. W., Esser B., Dumele O. (2023), Antiaromatic Covalent Organic Frameworks Based on Dibenzopentalenes, J. Am. Chem. Soc., 145, 2840–2851 (DOI: 10.1021/jacs.2c10501).
- (50) Liu H., Huang W., Yu Y., Chen D. (2023), Lightning-Rod Effect on Nanowire Tips Reinforces Electroporation and Electrochemical Oxidation: An Efficient Strategy for Eliminating Intracellular Antibiotic Resistance Genes, ACS Nano, 17, 3037–3046 (DOI: 10.1021/acsnano.2c11811).
- (51) Peng H., Jiang B., Li F., Gong J., Zhang Y., Yang M., Liu N., Ma L. (2023), Single-Crystal-Structure Directed Predesign of Cationic Covalent Organic Polymers for Rapidly Capturing ⁹⁹TcO₄⁻, Chem. Mater., 35, 2531-2540 (DOI: 10.1021/acs.chemmater.2c03812).
- (52) Chang X., Lin C. W., Huang A., El-Kady M. F., Kaner R. B. (2023), Molecular Engineering of Hierarchical Conducting Polymer Composites for Highly Stable Supercapacitors, Nano Lett., 23, 3317-3325 (DOI: 10.1021/acs.nanolett.3c00284).
- (53) Jadhav R. G., Singh D., Mobin S. M., Das A. K. (2020),

Engineering of Electrodeposited Binder-Free Organic-Nickel Hydroxide Based Nanohybrids for Energy Storage and Electrocatalytic Alkaline Water Splitting, Sustain. Energy Fuels, 4, 1320–1331 (DOI: 10.1039/c9se00483a).

- (54) Han R., Ren J., Zhou Z., Chen G., Li Q. (2023), Preparation of High - k Polymeric Composites Based on Low - k Boron Nitride Nanosheets with High-Connectivity Lamellar Structure, ACS Appl. Mater. Interfaces, 15, 34064-34074 (DOI: 10.1021/acsami.3c06143).
- Gao J., Qin J., Chang J., Liu H., Wu Z. S., Feng L. (2020), NH₃ (55)Sensor Based on 2D Wormlike Polypyrrole/Graphene Heterostructures for a Self-Powered Integrated System, ACS Interfaces. 12, 38674-38681 Appl. Mater. (DOI: 10.1021/acsami.0c10794).
- (56) Kwon K. C., Suh J. M., Lee T. H., Choi K. S., Hong K., Song Y. G., Shim Y., Shokouhimehr M., Kang C., Kim S. Y., Jang H. W. (2019), SnS₂ Nanograins on Porous SiO₂ Nanorods Template for Highly Sensitive NO₂ Sensor at Room Temperature with Excellent Recovery, ACS Sensor, 4, 678–686 (DOI: 10.1021/acssensors.8b01526).
- (57) Tai H., Jiang Y., Xie G., Yu J., Chen X., Ying Z. (2008), Influence of Polymerization Temperature on NH₃ Response of PANI/TiO₂ Thin Film Gas Sensor, Sensors Actuators, B Chem., 129, 319–326 (DOI: 10.1016/j.snb.2007.08.013).
- (58) Hasani A., Sharifi Dehsari H., Asghari Lafmejani M., Salehi A., Afshar Taromi F., Asadi K., Kim S. Y. (2018), Ammonia-Sensing Using a Composite of Graphene Oxide and Conducting Polymer, Phys. Status Solidi - Rapid Res. Lett., 12, 1800037 (DOI: 10.1002/pssr.201800037).
- He J., Liang B., Yan X., Liu F., Wang J., Yang Z., You R., Wang (59) C., Sun P., Yan X., Lin H., Kang B., Wang Y., Lu G. (2021), A **TPA-DCPP** Semiconductor Organic Film-Based Room Temperature NH₃ Sensor for Insight into the Sensing Properties, Sensors В Chem., 327, 128940 Actuators, (DOI:

10.1016/j.snb.2020.128940).

- (60) Li P., Xu H., Liu F., Shi J., Gao X., Li J. (2023), Room-Temperature NH₃ Sensors Based on Polyaniline-Assembled Graphitic Carbon Nitride Nanosheets, ACS Appl. Nano Mater., 6, 5145–5154 (DOI: 10.1021/acsanm.2c04940).
- (61) Li P., Li J., Liu F., Shi J., Gao X., Xu H. (2023), Cu-Loaded Polyaniline-Coated MoO₃ Nanowire Nanohybrids for High-Sensitivity NH₃ Sensing at Room Temperature, ACS Appl. Nano Mater., 6, 17423–17432 (DOI: 10.1021/acsanm.3c02270).
- (62) Singh V. K., Verma A., Kumar P., Mishra V. N. (2023), Solution-Processed, Highly-Efficient Organic Field-Effect Transistor Based Hydrogen Sulfide Gas Sensor at Sub-Ppm Regime, IEEE Sens. J., 23, 16600–16607 (DOI: 10.1109/JSEN.2023.3288932).
- (63) Sagdullina D., Lukashkin N., Parfenov A., Lyssenko K., Troshin P. (2020), Highly Sensitive OFET-Based Gas Sensors Using Fluorinated Naphthalenediimide Semiconductor Films, Synth. Met., 260, 116289 (DOI: 10.1016/j.synthmet.2019.116289).
- (64) Lerner Yardeni J., Amit M., Ashkenasy G., Ashkenasy N. (2016), Sequence Dependent Proton Conduction in Self-Assembled Peptide Nanostructures, Nanoscale, 8, 2358–2366 (DOI: 10.1039/c5nr06750b).
- (65) Tanaka R., Yamamoto H., Shono A., Kubo K., Sakurai M. (2000), Proton Conducting Behavior in Non-Crosslinked and Crosslinked Polyethylenimine with Excess Phosphoric Acid, Electrochim. Acta, 45, 1385–1389 (DOI: 10.1016/S0013-4686(99)00347-3).
- (66) Park H., Kim D. H., Ma B. S., Shin E., Kim Y., Kim T. S., Kim F. S., Kim I. D., Kim B. J. (2022), High-Performance, Flexible NO₂ Chemiresistors Achieved by Design of Imine-Incorporated n-Type Conjugated Polymers, Adv. Sci., 9, 2200270 (DOI: 10.1002/advs.202200270).
- (67) Sardana S., Kaur H., Arora B., Aswal D. K., Mahajan A. (2022), Self-Powered Monitoring of Ammonia Using an MXene/TiO₂/Cellulose Nanofiber Heterojunction-Based Sensor Driven by an Electrospun Triboelectric Nanogenerator, ACS

Sensors, 7, 312–321 (DOI: 10.1021/acssensors.1c02388).

- (68) Niu F., Shao Z. W., Tao L. M., Ding Y. (2020), Covalent Triazine-Based Frameworks for NH₃ Gas Sensing at Room Temperature, Sensors Actuators, B Chem., 321, 128513 (DOI: 10.1016/j.snb.2020.128513).
- (69) Tao L. M., Niu F., Zhang D., Wang T. M., Wang Q. H. (2014), Amorphous Covalent Triazine Frameworks for High-Performance Room Temperature Ammonia Gas Sensing, New J. Chem., 38, 2774–2777 (DOI: 10.1039/c4nj00476k).
- (70) Achary L. S. K., Kumar A., Barik B., Nayak P. S., Tripathy N., Kar J. P., Dash P. (2018), Reduced Graphene Oxide-CuFe₂O₄ Nanocomposite: A Highly Sensitive Room Temperature NH₃ Gas Sensor, Sensors Actuators, B Chem., 272, 100–109 (DOI: 10.1016/j.snb.2018.05.093).
- (71) Dehsari H. S., Gavgani J. N., Hasani A., Mahyari M., Shalamzari E. K., Salehi A., Taromi F. A. (2015), Copper(II) Phthalocyanine Supported on a Three-Dimensional Nitrogen-Doped Graphene/ PEDOT-PSS Nanocomposite as a Highly Selective and Sensitive Sensor for Ammonia Detection at Room Temperature, RSC Adv., 5, 79729–79737 (DOI: 10.1039/c5ra13976g).
- (72) Stulik J., Slauf J., Polansky R., Mergl M., Kalbac M. (2022), Highly Sensitive Room-Temperature Ammonia Sensors Based on Single-Wall Carbon Nanotubes Modified by PEDOT, IEEE Sens. J., 22, 3024–3032 (DOI: 10.1109/JSEN.2022.3142405).
- (73) Singh S., Deb J., Sarkar U., Sharma S. (2021), MoS₂/MoO₃ Nanocomposite for Selective NH₃ Detection in a Humid Environment, ACS Sustain. Chem. Eng., 9, 7328–7340 (DOI: 10.1021/acssuschemeng.1c01527).
- Jin L., Wu C., Wei K., He L., Gao H., Zhang H., Zhang K., Asiri A. M., Alamry K. A., Yang L., Chu X. (2020), Polymeric Ti₃C₂T XMXene Composites for Room Temperature Ammonia Sensing, ACS Appl. Nano Mater., 3, 12071–12079 (10.1021/acsanm. 0c02577).
- (75) Seekaew Y., Lokavee S., Phokharatkul D., Wisitsoraat A.,

Kerdcharoen T., Wongchoosuk C. (2014), Low-Cost and Flexible Printed Graphene-PEDOT:PSS Gas Sensor for Ammonia Detection, Org. Electron., 15, 2971–2981 (DOI: 10.1016/j.orgel. 2014.08.044). Chapter 5 Fabricated Chemiresistive Sensor for Detection of Ethanol Using NDICY-ZnO Nanohybrid

5.1 Introduction

Organic-inorganic hybrid-based gas sensors are gaining enormous attention for providing high selectivity and room temperature operation which are the major limitations associated with the metal oxide-based sensors [1,2]. The organic constituent of the hybrid material brings remarkable selectivity while the inorganic part exhibits long-term stability [3,4]. In this regard, organic-inorganic nanohybrid materials can be used as efficient materials for gas sensing applications [3,5]. The synergistic assembly of organic-inorganic nanohybrid materials-based sensors provide better efficiency towards gas sensing performance due to their large effective surface area, more accessible active sites, and better conducting properties [4,6]. In addition, the interface of organicinorganic nanohybrid makes the material more promising for gas sensing applications [7]. Various organic-inorganic nanocomposites such as polyaniline (PANI)-TiO₂, polypyrrole-SnO₂, etc have been explored till now for sensing applications. Pang et al have reported the PANI-TiO₂ nanocomposite for ammonia sensing [8]. In another report, the PANI-SnO₂ nanocomposite was investigated for ethanol and acetone sensing. Furthermore, Bagchi and Ghanshyam reported the polypyrrole coated tin-oxide for enhanced ammonia sensing [9].

An organic segment plays a crucial role in organic-inorganic nanohybrid for gas sensing performance. Among various organic compounds, naphthalene diimide (NDI) is gaining much more attention owing to its large electron affinity, excellent electron mobility, and good chemical and thermal stability [10,11]. In addition, NDI also possesses π conjugation with varying imide (longitudinal) and core (lateral) positions with specific functional groups which provides remarkable selectivity towards particular target analyte [12,13]. Among different amino acids, tyrosine (Y) based peptides form higher-order self-assembled structures, and the redox property of both also facilitates the transfer of electrons [14]. In addition, long aliphatic chains can also drive the formation of higher-order self-assembled structures. The alkyl chain balances the rigidity and flexibility and plays a crucial role in hydrophobic interaction. Moreover, the alkyl chain exhibits dimension stability, good dielectric properties, and low-temperature impact resistance [15,16]. Among many metal oxides, zinc oxide (ZnO) is widely studied as a gas sensor material, because of its wide band gap ($E_g \sim 3.37 \text{ eV}$), intrinsic n-type conductivity, high thermal and chemical stability, large surface area, and room temperature large exciton binding energy of 60 meV [17]. Therefore, the introduction of metal oxide particularly ZnO enhances stability due to the presence of synergistic behavior in the organic-inorganic nanohybrids. The additional self-doping of metal oxides and NDI units could further improve the electron transportation nature and make more compatible material for sensing processes at mild conditions [18].

Volatile organic compounds (VOCs) are encountered in many activities such as painting colors, cutting grasses, cooking, and oil refinery [19,20]. The uncontrolled release of VOCs from anthropogenic sources has a negative influence on ambient air [21]. High concentration and long-term exposure to VOCs can cause damage to nerves and respiratory system [22,23]. Among the various VOCs, the detection and monitoring of ethanol concentration exposure are crucial in different areas, such as the prevention of drunken driving, analysis of exhaled breath, maintaining food quality, detection in biomedical and chemical processes in pharmaceutical industries [24,25]. The standard limit of ethanol in the environment is 1000 ppm according to data released by the Occupational Safety and Health Administration (OSHA) and National Institute for Occupational Safety and Health (NIOSH) [25].

In this work, I have synthesized the NDICY followed by the addition of ZnO precursor in NDICY to synthesize NDICY-based zinc oxide (NDICY-ZnO) nanohybrid using facile one-pot hydrothermal method. The NDICY-ZnO nanohybrid material is characterized by SEM, TEM, FTIR, X-ray photoelectron spectroscopy (XPS), and Brunauer-Emmett-Teller (BET) analysis. The fabricated NDICY-ZnO sensor has excellent selectivity towards ethanol compared to other interfering VOCs and gases as well as investigated for ethanol sensing at room temperature. The sensing mechanism of NDICY-ZnO nanohybrid towards ethanol is also explained in detail.

5.2 Aims and Objectives

The aims and objectives of the current work are mentioned as follows;

- To synthesize an NDI-based dipeptide containing a 6-amino caproic acid alkyl chain (C) and tyrosine (Y) to enhance the self-assembly of the material.
- (ii) To synthesize NDICY-ZnO nanohybrid via a simple hydrothermal method.
- (iii) To study the presence of the functional group, crystalline behavior, thermal stability, and surface area of NDICY-ZnO nanohybrid.
- (iv) To evaluate the self-assembled morphology of the NDICY-ZnO nanohybrid.
- (v) To investigate the sensing performance of NDICY-ZnO nanohybrid at 27 °C.
- (vi) To investigate the effect of humidity, different concentrations, and the presence of interfering gases on the response of ethanol.
- (vii) To investigate the plausible mechanism of the sensing response of NDICY-ZnO nanohybrid towards ethanol.

5.3 Experimental Section

5.3.1 Materials and Methods

1,4,5,8-Naphthalenetetracarboxylic dianhydride was purchased from Aldrich. 6-Aminocaproic acid, L-tyrosine Sigma (Y), N.Ndiisopropylcarbodiimide (DIPC), 1-hydroxybenzotriazole (HOBt) and Zn(NO₃)₂.6H₂O were purchased from SRL, Mumbai and used without any purification. All the solvents were purchased from Merck and dried using the standard procedures. TLC was used to observe the progress of the reactions on aluminium plates coated with Merck Silica gel 60 F254. All intermediates and final compound were purified by flash chromatography (Teledyne ISCO, USA; model: CombiFlash®Rf+) using silica gel (100-200 mesh). All ¹H and ¹³C NMR spectra were set down on Bruker Avance (400 MHz) instrument at 25 °C. Mass spectra were set down on Bruker instrument by using ESI positive mode. The NMR spectra of all intermediates and final products were analyzed by using MestReNova software. The NMR samples were prepared in DMSO- d_6 and CDCl₃ solvent. The chemical shift was expressed in the form of ppm (δ) relative to surplus solvents protons as internal standards (CHCl₃: δ 7.26, DMSO- d_6 : δ = 2.50 for 1H NMR; and CHCl₃: δ 77.00, DMSO- d_6 : δ 39.50 for ¹³C NMR).

5.3.2 Synthesis of the compounds

Scheme 5.1 Overall synthetic pathways for liquid phase synthesis of nucleopeptide



5.3.2.1 Synthesis of 6-((tert-butoxycarbonyl)amino)hexanoic acid (Boc-Cap-OH, 2)

2.0 g (15.25 mmol) of 6-aminocaproic acid was dissolved in 1,4-dioxane (10 mL) and neutralized with 1 N NaOH (10 mL). The reaction mixture was stirred under cooling conditions for 10 min. After that di-*tert*-butyl dicarbonate (4.65 gm, 21.35 mmol) was added and stirred for 12 h at 25 °C. After completion of the reaction, 1,4-dioxane was evaporated under reduced pressure and the solution was neutralized with 1 N HCl under cold conditions. The compound was extracted with ethyl acetate (3×30 mL). The extracted ethyl acetate was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The desired organic compound was obtained as a thick viscous liquid. Yield: 74% (2.6 g, 11.24 mmol); ¹H NMR (400 MHz, DMSO-*d*₆): 6.71 (s, 1H, -NH), 2.89-2.85 (m, 2H, Cap

2.88 2.287 2.287 2.287 2.287 2.287 2.287 2.287 2.287 2.287 2.216 0.216 2.216 0

CH), 2.18-2.15 (t, 2H, *J* = 5.9 Hz, Cap CH), 1.49-1.45 (m, 2H, Cap CH), 1.35 (s, 9H, (CH₃)₃), 1.33-1.30 (t, 2H, J = 6.1 Hz, Cap CH), 1.25-1.20 (m, 2H, Cap CH). ¹³C NMR (100 MHz, DMSO-*d*₆): 175.07, 156.21, 77.93, 34.25, 29.84, 28.88, 26.47 and 24.84. ESI-MS m/z: calcd. for C₁₁H₂₁NO₄Na, 254.1378 [M+Na]⁺; found 254.1439.





200 190 180 170 160 150 140 130 120 110 100 90 80 Chemical shift (ppm) 70 60 50 40 30 20 10 0

Figure 5.2 ¹³C NMR spectrum (100 MHz, DMSO-d₆) of Boc-Cap-OH (2).



Figure 5.3 ESI-MS spectrum of Boc-Cap-OH (2).

5.3.2.2 Synthesis of methyl (6-((tert-butoxycarbonyl)amino) hexanoyl)-L-tyrosinate (Boc-Cap-Y-OMe, 5)

A solution of Boc-Cap-OH 2 (2 g, 8.65 mmol) was dissolved in anhydrous DMF (4 mL) and stirred for 5 min under cooling condition. HOBt (1.63 g, 12.10 mmol) and N,N'-diisopropylcarbodiimide (1.53 g, 12.10 mmol) were added to reaction mixture and allowed to stir for 5 min. The hydrochloride salt of tyrosine methyl ester 4 (3.38 g, 17.3 mmol) was neutralized with saturated Na₂CO₃ solution and neutralized tyrosine methyl ester was extracted with ethyl acetate (3×30 mL). The organic part was dried over anhydrous Na2SO4 and evaporated under reduced pressure. The neutralized tyrosine methyl ester was added to the reaction mixture and allowed to stir for 12 h. After completion of the reaction, ethyl acetate (20 mL) was added to the reaction mixture and washed with 1 N HCl (3×50 mL), saturated Na₂CO₃ (3×50 mL) and brine solution (2×50 mL). The organic part was dried over anhydrous Na₂SO₄ and evaporated under reduced pressure to obtain 5. The crude product was purified using flash chromatography using silica gel (100-200 mesh) with EtOAc:hexane :: 6:4 as mobile phase to obtain desired Boc-Cap-Y-OMe. Yield: 80% (2.84 g, 6.95 mmol); ¹H NMR (400 MHz, DMSO-*d*₆): 7.5 (s, 1H, -OH of Tyr), 6.98-6.96 (d, 2H, *J* = 8.36 Hz, Tyr aromatic H), 6.83-6.81 (d, 2H, J = 8.12 Hz, Tyr aromatic H), 5.93-5.91 (d, 1H, J = 8 Hz, -NH), 4.89-4.87 (m, 1H, C^{α}H), 4.69 (s, 1H, NH), 3.78 (s, 3H, -OCH₃), 3.23-3.19 (m, 1H, $C^{\beta}H$ of Tyr), 3.04-3.01 (t, 2H, J = 6.7Hz, Cap CH), 2.90-2.84 (m, 1H, C^{β}H of Tyr), 2.20-2.09 (m, 2H, Cap CH), 1.48 (s, 9H, (CH₃)₃), 1.42-1.36 (m, 4H, Cap CH), 1.10-1.09 (t, 2H, Cap CH). ¹³C NMR (100 MHz, DMSO- d_6): $\delta = 172.86$, 172.80, 156.47, 156.10, 130.45, 127.79, 115.51, 113.74, 77.83, 54.32, 52.17, 36.54, 35.44, 29.77, 28.76, 26.33, 25.40. ESI-MS m/z: calcd. for C₂₁H₃₂N₂O₆Na, 431.2260 [M+Na]⁺; found 431.2084.



Figure 5.4 ¹H NMR spectrum (400 MHz, DMSO- d_6) of Boc-Cap-Y-OMe (5).



Figure 5.5 ¹³C NMR spectrum (100 MHz, DMSO- d_6) of Boc-Cap-Y-OMe (5).



Figure 5.6 ESI-MS spectrum of Boc-Cap-Y-OMe (5).

5.3.2.3 Synthesis of NDICY-OMe (7)

Naphthalene dianhydride (500 mg, 1.86 mmol) was dissolved in anhydrous DMF (10 mL) and allowed to stir for 15 min under inert condition. Boc-Cap-Y-OMe (4.5 g, 11.2 mmol) was stirred with trifluoroacetic acid (TFA) in 1,4-dioxane solvent and the reaction was continuously monitored by TLC. After the deprotection of Boc, excess solvent and TFA were evaporated under reduced pressure. The resulting solution was neutralized with DIPEA and reaction mixture was added into naphthalene dianhydride solution and allowed to stir for 12 h under inert condition at 100 °C. After the completion of the reaction, the resultant mixture was poured into ice water to obtain yellow precipitate. The yellow precipitate was collected using simple filtration process. The precipitate was further purified by flash chromatography using silica gel (100-200 mesh) with CHCl₃: EtOAc (1:9) as eluent solvent.

Yield: 63% (995 mg, 1.17 mmol); ¹H NMR (400 MHz, DMSO-*d*₆): 9.21 (s, 2H, -OH of Tyr), 8.61 (s, 4H, NDI aromatic CH), 8.21-8.20 (d, 2H, J = 6.12 Hz, NH), 6.96-6.94 (d, 4H, J = 6.56 Hz, Tyr aromatic CH), 6.64-6.63 (d, 4H, J = 6.56 Hz, Tyr aromatic CH), 4.35-4.34 (t, 2H, J = 4.96 Hz, C^aH of Tyr), 4.03-4.00 (t, 2H, J = 5.2 Hz, Cap CH), 3.55 (s, 6H, - OCH₃), 2.86-2.82 (d, 2H, J = 6.48 Hz, C^βH of Tyr), 2.73-2.63 (d, 2H, C^βH of Tyr), 2.11-2.08 (m, 4H, Cap CH), 1.64-1.62 (m, 4H, Cap CH), 1.51-1.48 (m, 4H, Cap CH), 1.29-1.24 (t, 4H, J = 5.44 Hz, Cap CH). ¹³C NMR (100 MHz, DMSO-*d*₆): 172.78, 172.63, 162.95, 156.41, 130.86, 130.37, 127.68, 126.62, 115.43, 54.29, 52.11, 36.50, 35.22, 27.70, 26.47,



 180
 170
 160
 150
 140
 130
 120
 110
 100
 90
 80
 70
 60
 50
 40
 30
 20
 10
 0

 Figure 5.8
 13C
 NMR
 spectrum
 (100
 MHz, DMSO-d₆) of NDICY-OMe

 (7).



Figure 5.9 ESI-MS spectrum of NDICY-OMe (7).

5.3.2.4 Synthesis of NDICY (8)

NDICY-OMe (500 mg, 0.59 mmol) was dissolved in 10 mL THF and stirred for 15 min at 70 °C. Further, 1 N HCl (20 mL) was added to the reaction mixture and allowed to stir at 70 °C for 48 h. Reaction progression was monitored using thin layer chromatography (TLC). After completion of the reaction, THF was evaporated under reduced pressure. After that concentrated part was poured into ice water. Compound 8 was precipitated out in water. Finally, compound 8 was filtered, washed with water and dried in oven at 60 °C. Yield: 74% (360 mg, 0.44 mmol); ¹H NMR (400 MHz, DMSO-*d*₆): 12.52 (s, 2H, H of COOH), 9.16 (s, 2H, OH of Tyr), 8.67 (s, 4H, NDI H), 8.04-8.02 (d, 2H, J = 7.92 Hz, NH), 6.99-6.97 (d, 4H, J = 7.8 Hz, Tyr H), 6.64-6.62 (d, 4H, J = 7.6 Hz, Tyr H), 4.32-4.14 (t, 2H, J = 4.9 Hz, C^{α}H of Tyr), 4.05-4.01 (t, 4H, J = 6.48 Hz, Cap CH), 2.89-2.85 (m, 2H, C^{β}H of Tyr), 2.73-2.65 (m, 2H, $C^{\beta}H$ of Tyr), 2.10-2.06 (t, 4H, J = 6.68 Hz, Cap CH), 1.63-1.61 (m, 4H, Cap CH), 1.49-1.47 (m, 4H, Cap CH), 1.29-1.27 (m, 4H, J =8Hz, Cap CH). ¹³C NMR (100 MHz, DMSO-*d*₆): 173.92, 172.82, 162.97, 156.45, 130.99, 130.58, 128.30, 126.58, 115.54, 54.34, 36.71, 35.55, 27.85, 26.68, 25.58. ESI-MS m/z: calcd for C44H45N4O12, 821.3034 [M+H]⁺; found 821.3360.



Figure 5.10 ¹H NMR spectrum (400 MHz, DMSO- d_6) of NDICY (8).



Figure 5.11 ¹³C NMR spectrum (100 MHz, DMSO-*d*₆) of NDICY (8).



Figure 5.12 ESI-MS spectrum of the NDICY (8).

5.3.2.5 Synthesis of the NDICY-ZnO Nanohybrid

The hydrothermal method was used for synthesizing the 1:50 NDICY-ZnO nanohybrid (Figure 5.13). In hydrothermal method, Zn(NO₃)₂.6H₂O (905 mg, 3.04 mmol) and hexamethylenetetramine (HMTA) (426 mg, 3.04 mmol) were taken in 10 mL milli-Q water and stirred continuously at 60 °C for 20 min. Then, 50 mg NDICY (0.060 mmol) was dispersed in water and added slowly to the above reaction mixture and allowed to stir for 30 min. After that, the dispersed mixture was transferred to the Teflon lined autoclave and heated in an oven at 180 °C for 12 h. After the completion of the reaction, the desired nanohybrid (NDICY-ZnO) was collected, filtered, and washed with milli-Q water and other organic solvents. Then, the nanohybrid residue was dried for 6 h at 60 °C. Finally, the NDICY-ZnO nanohybrid material was crushed into fine powder. The synthesis of 1:25 and 1:100 NDICY-ZnO nanohybrids has been discussed in the supporting file. In NDICY-ZnO nanohybrid, NDI is naphthalene diimide, C is six-aminocaproic acid, and Y is L-tyrosine. The self-assembly of NDICY-ZnO nanohybrid was displayed in Figure 5.14.



Figure 5.13 Schematic representations of the synthesis of NDICY-ZnO composite nanohybrid *via* hydrothermal method and fabrication of nanohybrid on the interdigitated electrode.



Figure 5.14 Schematic representation of self-assembled organic-inorganic nanohybrid.

5.3.2.6 Synthesis of the Zinc Oxide (ZnO)

ZnO was also synthesized using a hydrothermal technique. Here, Zn(NO₃)₂·6H₂O (500 mg, 1.6 mmol) and hexamethylenetetramine (HMTA) (235 mg, 1.6 mmol) were dissolved in 10 mL milli-Q water and stirred continuously at 60 °C for 20 min. After that, the reaction mixture was transferred to the Teflon lined autoclave and kept in the oven at 180 °C for 12 h. After the completion of the reaction, ZnO was collected, filtered and washed several times with milli-Q water and ethanol. Then, the ZnO residue was dried for 6 h at 60 °C. Finally, the ZnO was crushed into fine powder.

5.3.2.7 Synthesis of the mechanically grinded NDICY-ZnO Composite

The NDICY-ZnO composite was synthesized *via* mechanical grinding method. The NDICY and ZnO were taken in mortar pestle in a ratio of 1:50, which consists of 1 equivalent of NDICY and 50 equivalents of ZnO. The NDICY and ZnO were continuously grinded for 3 h at 25 °C. The resulting NDICY-ZnO composite was washed with water and

ethanol and dried in an oven for 6 h at 70 °C. Finally, the NDICY-ZnO composite was crushed into fine powder.

5.3.3 Characterization Technique

Mass spectra of the intermediates and products were recorded on Bruker micrOTOF-Q II mass spectrometer by positive mode electrospray ionization. ¹H NMR and ¹³C NMR of synthesized compounds were carried out on Bruker AV 400 MHz spectrometer using DMSO-d₆, CDCl₃, and TMS as the internal reference. The chemical shifts (δ) are expressed in parts per million (ppm) relative to TMS and peak multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). The crystalline nature of materials was characterized using X-ray powder diffraction (PXRD) (Rigaku SmartLab automated multipurpose X-ray diffractometer with Cu-K α X-radiation (λ = 1.54 Å)). Thermogravimetric analysis (TGA) was also performed to investigate the thermal stability of the material using a Mettler Toledo thermal analyzer under inert conditions, at a heating rate of 10 °C/min. The N₂ sorption experiment was performed to calculate the surface area and pore volume of the material using Autosorb iQ2. The surface morphology of the materials was analyzed using field emission scanning electron microscopy (FE-SEM). The high-resolution transmission electron microscopic (HR-TEM) image of the materials was analyzed using a JEOL electron microscope (model: JEM-2100) at an accelerating voltage of 200 kV. FT-IR spectra of materials were collected using Bruker (Tensor 27) FT-IR spectrophotometer. X-ray photoelectron spectroscopy (XPS) analysis was obtained on ThermoFisher Nexsa with an Al Kalpha source.

5.3.4 Gas Sensor Fabrication and Measurement

The NDICY-ZnO composite nanohybrid mixed with deionized (DI) water was subsequently drop-casted on interdigitated electrodes (IDEs, $1.5 \text{ cm} \times 1 \text{ cm}$) and dried in the oven for 24 h at 70 °C. The fabricated NDICY-ZnO nanohybrid sensing device was kept inside a sensing
chamber to perform sensing experiment at 27 °C. The different concentrations of VOCs were carried by the synthetic air through the bubbler to the sensing chamber. The concentrations of VOCs were varied by varying the synthetic air flow rate using mass flow controllers, MFC (model: Alicat®, MC 1slpm, USA). The resistance of the fabricated sensing device was monitored on Keithley-2612A source meter at applying constant voltage of 1 V. For the selectivity experiment of the sensing material, N₂ gas was exposed to the sensing chamber for 10 min to obtain the base resistance. In addition, the sensor performance was also investigated at different relative humidities (RH%) varying from 42 to 97%. The desired concentration of humidity was obtained using a saturated solution of different salts such as potassium carbonate (46% RH), sodium chloride (75% RH), and potassium sulfate (97% RH) [26]. The response of the nanohybrid sensor was obtained using the following equation:

$$R = \frac{R_a - R_g}{R_a} \times 100\% \tag{5.1}$$

where R_a and R_g are the resistance of the nanohybrid sensor in ambient air and during gas exposure respectively. The response and recovery time are defined as the time taken by the sensing material to reach 90% of the maximum response for adsorption of targeted gases and the time taken to reach 10% of the response for desorption of the targeted gas, respectively.

5.4 Results and Discussion

Herein, we have synthesized two dipeptide functionalized NDI-based ZnO nanohybrid (NDICY-ZnO) using the hydrothermal method. The synthesized material was well characterized through several characterization techniques. Powder X-ray diffraction patterns of NDICY, ZnO, and NDICY-ZnO are illustrated in **Figure 5.15a**. The ZnO exhibits the peaks at $2\theta = 31.7^{\circ}$, 34.49° , 36.3° , 47.6° , and 56.69° corresponding to (100), (002), (101), (102) and (103) planes, respectively

(compared with JCPDS No.36-1451) which indicate the crystalline nature of ZnO [27]. The NDICY shows a broad peak at $2\theta = 15$ to 28° in the PXRD pattern, which indicates the amorphous nature of the organic compound. A small broad peak at $2\theta = 10.5^{\circ}-11.5^{\circ}$ along with $2\theta =$ 31.7° , 34.49° , 36.3° , 47.6° , and 56.69° in NDICY-ZnO PXRD pattern indicates the composite behavior of NDICY and ZnO. The PXRD pattern of NDICY-ZnO confirms the formation of organic-inorganic composite nanohybrid [5].



Figure 5.15 (a) PXRD patterns of NDICY, ZnO, and NDICY-ZnO nanohybrid. (b) FTIR spectra of NDICY and NDICY-ZnO nanohybrid. (c) TGA curves of NDICY and NDICY-ZnO and (d) table containing the amount (%) of ZnO in NDICY-ZnO nanohybrid was determined by TGA using the given formula.

Fourier transform infrared (FT-IR) analysis of the composite material further supports the formation of NDICY-ZnO nanohybrid. An FTIR peak appeared at 1511, 1646, and 1701 cm⁻¹ for NDICY, ascribed to NH (amide II), C=O (amide I), and C=O (COOH) stretching frequencies, respectively [28,29]. The peak of C=O of COOH is shifted to 1701 cm⁻¹

in NDICY-ZnO (Figure 5.15b), which shows the interaction of COOH functional group with ZnO. Thus, the FT-IR spectrum of NDICY-ZnO determines the non-covalent interaction between NDICY and ZnO, which confirms the formation of nanohybrid [30]. Thermogravimetric analysis (TGA) was performed to study the thermal stability of NDICY, ZnO, and NDICY-ZnO (Figure 5.15c). The TGA curves of NDICY, ZnO, and NDICY-ZnO clearly show different thermal behavior. At 800 °C, the residual masses (%) of NDICY, ZnO, and NDICY-ZnO are found as 2.3%, 98.2%, and 63.9%, respectively, which highlights the higher thermal stability behavior of ZnO than NDICY-ZnO and NDICY. An amount of 64.2% ZnO is present in the NDICY-ZnO nanohybrid (Figure 5.15d) at 800 °C. Therefore, the higher stability of NDICY-ZnO nanohybrid than NDICY is attributed to the low content of NDICY in the nanohybrid and also due to the synergistic effect of NDICY and ZnO. Therefore, the aforementioned TGA analysis reveals that fabricated NDICY-ZnO nanohybrid is enough thermally stable than NDICY and used as proposed sensor at 27 °C [31].



Figure 5.16 BET surface area graphs of (a) NDICY, (b) ZnO and (c) NDICY-ZnO nanohybrid inset with pore diameter curve calculated by

NL-DFT method and (d) table containing BET surface area and pore volume of NDICY, ZnO and NDICY-ZnO nanohybrid.

To evaluate the surface area and porosity of NDICY, ZnO, and NDICY-ZnO nanohybrid, the BET N_2 gas adsorption/desorption isotherm experiment was performed (**Figure 5.16a-5.16c**). The BET graph of the NDICY-ZnO shows a type II isotherm [32]. The calculated BET surface areas of NDICY, ZnO, and NDICY-ZnO are 10.6, 24.4, and 38.08 m²/g, respectively. However, the surface area of NDICY-ZnO is increased by 3.6 times than the surface area of NDICY. The pore size distribution calculation is accomplished using the DFT method of the NDICY, ZnO, and NDICY-ZnO (**inset Figure 5.16**). **Figure 5.16d** represents a summary of BET surface area and pore volume of the NDICY, ZnO, and NDICY-ZnO.



Figure 5.17 (a) SEM image of NDICY. SEM images of NDICY-ZnO nanohybrids at different molar concentration (b) 1:25, (c) 1:50 and (d) 1:100 inset with EDS analysis of NDICY-ZnO nanohybrid. (e) Elemental mapping of NDICY-ZnO showing uniform distribution of elements in (a) 1:25, (b) 1:50 and (c) 1:100 molar ratio.

The surface morphology of NDICY and NDICY-ZnO was analyzed using SEM analysis (**Figure 5.17a-5.17d**). The SEM image of NDICY shows the fiber type of morphology (**Figure 5.17a**). Non-covalent interactions such as Van der Waals, H-bonding, and π - π stacking interactions among organic moieties of NDICY can be the reason for self-assembled fiber morphology. The SEM images of NDICY-ZnO at different molar ratios show the homogenous flakes-like morphology throughout the surface (**Figure 5.17b-5.17d**). An EDS spectrum (**inset Figure 5.17b-5.17d**) exhibits a strong signal for Zn and O elements, which represents the existence of an inorganic part in NDICY-ZnO. Similarly, a strong EDS signal corresponding to elemental C, O, and N represents the existence of organic moiety in NDICY-ZnO nanohybrid. The elemental mapping of NDICY-ZnO nanohybrid at 1:25, 1:50, and 1:100 shows the homogenous distribution of elements (C, N, O, and Zn) over the surface (**Figure 5.17e**). The surface morphology of ZnO was also studied, which shows rod-like morphology and EDS pattern of ZnO indicates the presence of Zn and O (**Figure 5.18a-5.18d**).



Figure 5.18 (a) SEM image, (b) EDX, (c) and (d) Elemental mapping of ZnO.

HRTEM image of NDICY-ZnO corroborates the formation of flake-like morphology (**Figure 5.19a**). The lattice fringes in different directions are observed for ZnO indicating the polycrystalline nature of ZnO (**Figure 5.19b**). Bright spots in the selected area electron diffraction (SAED) pattern of NDICY-ZnO (**Figure 5.19c**) reveal the polycrystalline nature of NDICY-ZnO [5]. HRTEM of ZnO was also performed to confirm the rod shape of ZnO (**Figure 5.19d**). The lattice fringes are observed in ZnO indicating the wurtzite crystal structure of ZnO (**Figure 5.19e**) and bright spots in the SAED pattern of ZnO reveal the polycrystalline nature of ZnO (**Figure 5.19f**).



Figure 5.19 (a) TEM image of NDICY-ZnO. (b) HRTEM image of NDICY-ZnO. (c) SAED pattern of NDICY-ZnO. (d) TEM of ZnO. (e) HRTEM of ZnO and (f) SAED pattern of ZnO.

The surface composition of NDICY-ZnO nanohybrid was further investigated by XPS (**Figure 5.20**). **Figure 5.20a** depicts the XPS survey spectrum of NDICY-ZnO nanohybrid, indicating the existence of C, N, O, and Zn elements. The Zn 2p components of NDICY-ZnO nanohybrid show higher binding energies than the Zn 2p binding energies of as synthesized ZnO (**Figure 5.20b**). The slight deviation in binding energies may be attributed to two main possible reasons: (1) the changes in chemical environment interactions with the surface elements and (2) the variation of texture coefficients with the morphology of NDICY-ZnO nanohybrid. The deconvoluted Zn 2p core-level spectrum of the NDICY-ZnO nanohybrid shows two peaks located at about 1045.1 and 1022 eV that are attributed to Zn 2p_{1/2} and Zn 2p_{3/2}, respectively.

These higher binding energies of Zn 2p region indicate that the oxidation state of Zn in the flakes surface of the nanohybrid is +2. The binding energy difference between the Zn $2p_{1/2}$ and Zn $2p_{3/2}$ is 23 eV for the NDICY-ZnO [33,34]. The XPS spectrum of O 1s core-level of NDICY-ZnO indicates five different forms of oxygen atoms (**Figure 5.20c**). The

peaks that appeared at 529.7 and 531.2 eV are indicated to O²⁻ ions in the Zn-O and Zn-OH bonds of the NDICY-ZnO [35]. On the other hand, the remaining three peaks at 531.4, 532.01, and 532.2 eV of the O1s XPS spectrum correspond to different C=O bonds which originated from the surface adsorbed organic (NDICY) molecules [36]. The deconvoluted C 1s spectrum in NDICY-ZnO shows seven different peaks (Figure **5.20d**). The peaks at 283.7 and 284.9 eV correspond to C-C bonds (sp²) and sp³ carbon). The peaks at 285.9 and 286.4 eV originate from the -C=O and C-N bonds attached to the NDI core in the hybrid. The peak at 288.7 eV is attributed to -C(=O) NH- or $-CO_2^-$ bonds. The binding energy peak that appeared at 289.4 eV is attributed to the free -COOH groups in the NDICY-ZnO. The NDI imide core shows one extra peak at 292.4 eV (π - π * satellite) due to the presence of aromatic cores [37,38]. The deconvoluted N 1s spectrum constitutes of three peaks centered at 400, 400.5, and 399.5 eV, which attribute to C-N of amide and C-N imide bonds, respectively (Figure 5.20e) [39,40]. This spectrum further verifies the existence of Zn, O, N, and C in NDICY-ZnO and interactions between NDICY and ZnO.



Figure 5.20 (a) XPS survey spectra of NDICY-ZnO. Deconvoluted XPS spectra for the element of (b) Zn 2p, (c) C1s, (d) O1s, and (e) N1s in NDICY-ZnO nanohybrid.

The chemical composition of ZnO rods was investigated by XPS analysis. The XPS survey spectrum of ZnO (**Figure 5.21**) indicates the existence of Zn and O elements. The Zn 2p components of ZnO shows binding energies at about 1044.3 and 1021.2 eV, attributed to Zn $2p_{1/2}$ and Zn $2p_{3/2}$, respectively [41]. These binding energies of Zn 2p region indicate the +2 oxidation state of Zn in rod surface of the ZnO. The XPS spectrum of O 1s core-level appeared at 531.2 eV, ascribed to the oxygen vacancy in ZnO [41]. This result verifies the existence of Zn and O in ZnO.



Figure 5.21 XPS spectra of (a) ZnO. (b) Deconvoluted XPS spectra of (b) Zn 2p and (c) O1s.

5.4.1 Current-voltage (I–V) analysis

An *I-V* characteristic of NDICY-ZnO was performed at 27 °C from -10 to +10 V. **Figure 5.22a** shows the *I-V* profile of the NDICY-ZnO. Linear *I-V* curve of the NDICY-ZnO is observed that indicates the Ohmic behavior [42]. Moreover, the output current in nano ampere for the applied suggests its potential as a low-power device which is favorable for portable sensor applications. The linear *I-V* response of the NDICY-ZnO encourages us to investigate the gas-sensing behavior of the nanohybrid.

5.4.2 Ethanol Sensing Properties of the NDICY-ZnO Nanohybrid The sensing experiments have been carried out with NDICY, ZnO, and NDICY-ZnO at 500 ppm ethanol concentration at 27 °C (Figure 5.22b). The response of NDICY-ZnO nanohybrid exhibits 66.4% with 450 and 500 s response and recovery time (Figure 5.22c), respectively whereas, individual organic and inorganic components i.e. NDICY and ZnO exhibit 17.8% and 19.6% responses, respectively with almost similar response and recovery time (τ_{res}/τ_{rec}). The increase in response for nanohybrid is attributed to the synergistic effect of organic and inorganic components. Interestingly, this high response is observed at low temperatures (27 °C) which is a major limitation associated with metal oxide-based sensors. Further, the ethanol sensing performance was observed at different molar ratios of 1:25, 1:50, and 1:100 of the NDICY and ZnO components. Figure 5.22d clearly depicts that 1:50 molar ratio of the NDICY-ZnO nanohybrid exhibits the highest response of 66.4% whereas 1:25 and 1:100 exhibit 10.1 and 10.4% response to 500 ppm ethanol, respectively. Therefore, the gas sensing experiments were investigated and measured using a 1:50 molar ratio of the organic and inorganic components of NDICY-ZnO.

The response of NDICY-ZnO composite synthesized *via* mechanical grinding method towards ethanol was studied at 500 ppm concentration under the same experimental conditions. The mechanically grinded NDICY-ZnO composite exhibits a maximum response of 44% with response and recovery time of 450 and 640 sec, respectively (**Figure 5.22e**). In this case, the mechanochemical synthesis was unable to create a highly homogeneous composite [43], which could lead to weak interfacial contacts between NDICY and ZnO and result in a weak synergistic effect compared to hydrothermally synthesized NDICY-ZnO nanohybrid. Therefore, mechanically grinded NDICY-ZnO composite-based sensor shows a little lower response to ethanol as compared to the hydrothermal method.



Figure 5.22 (a) *I-V* response of NDICY-ZnO nanohybrid at 27 °C. (b) Single-cycle response of ethanol when exposed to NDICY, ZnO and NDICY-ZnO sensing layer. (c) Dynamic response-recovery curve of the NDICY-ZnO nanohybrid sensor. (d) Response of ethanol (500 ppm) at different molar concentrations of NDICY and ZnO. (e) Dynamic response of ethanol of the mechanical grinded NDICY-ZnO composite-based sensor to 500 ppm at 27 °C and (f) Response/recovery variation at different concentrations of ethanol vapors.

The response of NDICY-ZnO based sensor was evaluated at different concentrations from 50 to 500 ppm of ethanol. **Figure 5.22f** demonstrates that as ethanol concentration is increased from 50 to 500 ppm, the response of the sensing material is also increased from 33 to

66.4%. The NDICY-ZnO based sensor response is double as the ethanol concentration is varied from 50 to 500 ppm. The sensing material shows a complete recovery when NDICY-ZnO was exposed to 500 ppm of ethanol but in the case of lower (50 and 200 ppm) concentrations of ethanol, incomplete recovery is observed. One of the possible reasons for incomplete recovery at lower concentrations is the difficulty in desorption of ethanol molecules from the NDICY-ZnO surface and resistance of a sensing layer was recovered by exposing a synthetic air to the sensing chamber [44].



Figure 5.23 (a) Humidity effect on the sensing layer when ethanol vapors were exposed at 27 °C. (b) The selectivity of ethanol among different interfering gases and VOCs. (c) The repeatability study of the NDICY-ZnO sensor at 500 ppm of ethanol vapors and (d) the long-term stability of ethanol response was studied for 90 days.

Humidity is one of the crucial parameters in sensor performance, especially when the sensing experiments are carried out in an ambient environment. Therefore, the response of the NDICY-ZnO sensor towards 500 ppm ethanol was investigated under 46%, 75%, and 97% relative humidity (RH). The response at different RH of 46%, 75%, and 97%

were recorded as 66.4%, 75.4%, and 83.6%, respectively (**Figure 5.23a**). The effect of lower RH below the atmospheric humidity is not significant therefore, response at lower humidity is not considered here. One interesting observation from this study is that sensor response towards ethanol increases on increasing the RH. The possible reason could be that the adsorbed water molecules on the surface of NDICY-ZnO increase the decomposition rate of ethanol and stabilize the charge after cleavage of ethanol bonds [45].



Figure 5.24 Reproducibility curve of (a) 1:25, (b) 1:50 and (c) 1:100 NDICY-ZnO based sensors towards 500 ppm ethanol.

The selectivity of the NDICY-ZnO nanohybrid sensor was evaluated by exposing different VOCs (ethanol, methanol, benzene, and aniline) and gases (NO₂, H₂S, and CO₂) to the sensing material with a concentration of 500 ppm except H₂S and NO₂ which were exposed at 100 ppm. **Figure 5.23b** demonstrates that NDICY-ZnO based sensor exhibits a high selectivity towards ethanol (66.4%) among other VOCs and gases such as methanol (9.6%), benzene (9.6%), aniline (10%), NO₂ (10.3%), H₂S (10%), CO₂ (9.7%), acetone (10.2%), and formaldehyde (10.4%) at

27 °C. The selectivity of the VOCs and gases depends on the interaction of the targeted gas and sensing material. Benzene, aniline, NO₂, and CO₂ contain double bond while ethanol contains single bonds, which shows different chemical bonding properties with the sensing layer. However, ethanol and methanol both are electron donating species but ethanol shows a higher response than methanol. The possible reason for the highest response towards ethanol is due to its lower Feshbach resonance energy than that of methanol. However, it has already been reported that lower the Feshbach energy, the easier the dissociation of molecules and the better the electron-donating ability. The Feshbach energy required for dissociation of ethanol is 8.2 eV whereas for methanol it is 10.2 eV, which is comparatively higher than that of ethanol [46,47].

The repeatability of NDICY-ZnO nanohybrid sensor's performance was examined by exposing 500 ppm of ethanol for three consecutive cycles. The sensor significantly recovered to its base value in each cycle without any drift, which signify the highly repetitive nature of the NDICY-ZnO sensor (Figure 5.23c). The average time of response and recovery remains similar for three cycles. Another parameter of the sensor was investigated to test sensors performance for a longer period of time. Figure 5.23d displays the durability of a NDICY-ZnO sensor in ambient condition. The response of the NDICY-ZnO based sensor was examined to 500 ppm ethanol after every ten days for 90 days at 27 °C. The results do not show significant change in the sensor response, which suggests good long term-stability of the sensor at atmospheric conditions. In addition, the reproducibility of the sensing performance was investigated for each hybrid composition considering four devices for each hybrid composition and tested in the same sensing environment (Figure 5.24). Interestingly, no significant deviation was observed in the sensing performance of each hybrid composition. As a result, these hybrid samples exhibit great reproducibility. The sensing performance of the NDICY-ZnO nanohybrid-based sensor was compared with available previous reports. Various parameters of this work such as response, concentration, and operating temperature are compared with related

185

literature (**Table 5.1**). **Table 5.1** depicts that the NDICY-ZnO-based sensor shows good sensitivity to ethanol as compared to other reported literature.

S. No.	Materials	Respon se	Ethanol Concentr	Operating Temperat	Refere nce
			ation (ppm)	ure (°C)	
1.	NDICY-ZnO nanohybrid	66.4%	500	RT	This work
2.	ZnO nano-tips	58%	200	325	48
3.	ZnO/MWNT Film	7.3%	500	RT	49
4.	Pd/ZnO	50%	300	RT	50
5.	In ₂ O ₃ -decorated NiO	9.76	5	350	51
6.	Methylammoni um lead iodide (MAPbI ₃)	3.8	10000	RT	52
7.	BPTS @ (PEDOT:PSS)	1.4	2000	RT	53

Table 5.1 Comparative study of various ethanol gas sensors

The sensing results shown above reveal that the NDICY-ZnO nanohybrid sensor exhibits the highest response towards ethanol gas at 27 °C, which shows its potential for real-time application. In general, the mechanism of VOCs and gas sensing is interpreted by the change in electrical resistance which is due to the transfer of electrons during the interaction of the sensing layer with targeted VOCs and gases.

The synergistic behavior of NDICY-ZnO nanohybrid provides excellent properties, large surface area, ultraselectivity, and electrical conductivity at 27 °C. The NDICY-ZnO response toward ethanol can be demonstrated on the basis of the depletion layer model. During the sensing experiment, the NDICY-ZnO-based sensor when comes in contact with air, and oxygen molecules get adsorbed on the surface and ionized to form oxygen anion (O_2^-) by capturing free electrons from the conduction band of the sensing layer. As a result, a thick depletion layer is created and the resistance of the layer increases, as shown in **Figure 5.25** [54]. The reaction mechanism of the formation of oxygen anions is given below:

$$O_2(g) \to O_2(ads) \tag{5.2}$$

$$O_2(ads) + e^- \to O_2^-(ads)$$
 (5.3)

Scheme 5.2 Schematic diagram of the mechanism of ethanol sensing at room temperature when exposed to NDICY-ZnO nanohybrid sensing layer



 $\bullet \bullet \bullet = \mathsf{O}_2, \ \bullet = \mathsf{O}_2^-, \ \bullet \bullet \bullet = \mathsf{CO}_2, \ \bullet \bullet \bullet = \mathsf{H}_2\mathsf{O}$

When the NDICY-ZnO based sensor is exposed to ethanol vapors (reducing VOC) and these ethanol molecules react with the adsorbed oxygen anion (O_2^-) on the surface. The ethanol molecules undergo dissociation and lead to the formation of byproducts CO_2 , H_2O , and free electrons [25]. These free electrons are attracted by the conduction band of NDICY-ZnO, which results in an increase in the electron density of the sensing layer, and the depletion layer width gets reduced. Hence, resistance of the sensing layer decreases which results in good sensing response and high selectivity to ethanol. The above reaction process is shown by the equation given below

$$2C_2H_5OH (ads) + 5O_2^- \rightarrow 4CO_2 + 4H_2O + 5e^-$$
 (5.4)

From **Figure 5.22b**, it can be clearly seen that NDICY-ZnO shows enhanced sensing response as compared to individual NDICY and ZnO. This could be due to the interaction between NDICY and ZnO which increases the surface area and number of active sites for adsorption of

ethanol molecules. Here, the NDI in nanohybrid has a major influence on the responses of the NDICY-ZnO sensor. NDI possesses a planar aromatic structure and has two electron-withdrawing imide groups at the core. NDIs are easily and reversibly reducible [11,55]. NDI being an electron-deficient aromatic moiety shows redox active behavior which makes them suitable for gas sensing applications. In the sensing experiment of ethanol, the decomposition of ethanol occurs in the sensing chamber, and CO₂, H₂O, and free electrons are formed as byproducts. NDI's electron deficiency nature attracts these free electrons produced during the decomposition of ethanol and decreases the resistance of the sensing layer (NDICY-ZnO), which results in a fast response and recovery of ethanol and ultra-selective behavior towards ethanol. The sensing experiments reveal that the synergistic behavior of nanohybrid is vital in the enhancement of ethanol response and also demonstrates that NDICY-ZnO can be used as sensing material for practical application with excellent features.

5.5 Conclusion

In summary, we have developed an NDICY-ZnO nanohybrid using a hydrothermal technique. The interaction between NDICY and ZnO was confirmed by FTIR spectroscopic techniques. The thermal stability, porosity, and morphology were obtained by TGA, BET, and SEM techniques, respectively. In this work, the NDICY-ZnO nanohybrid was fabricated on chemiresistive device to perform the gas sensing experiments. NDICY-ZnO nanohybrid-based sensor exhibited an excellent response of 66.4% to 500 ppm of ethanol at 27 °C when compared to the response of NDICY and ZnO (19% and 17%). A reasonable response and recovery time of 450 and 500 s were observed for 500 ppm of ethanol. Additionally, the based gas sensor is ultraselective towards 500 ppm of ethanol at 27 °C when compared with other interfering gases and VOCs. Moreover, the humidity had a positive effect on the ethanol response i.e. on increasing the relative humidity; the response of ethanol is also increased. Hence, the results shown above

suggest that NDICY-ZnO nanohybrid can be used as a promising sensing material for ethanol detection at 27 °C.

5.6 References

- Das P., Mondal B., Mukherjee K. (2020), Hierarchical Zinc Oxide Nano-Tips and Micro-Rods: Hydrothermal Synthesis and Improved Chemi-Resistive Response towards Ethanol, ACS Cent. Sci., 6, 1916–1937 (DOI: 10.1021/acscentsci.0c01046).
- (2) Zheng Y., Rong J., Zhu Y., Zhang T., Yang D., Qiu F. (2022), Construction of Highly Dispersed Active Sites in MoS₂/CuS/C Electrocatalyst Based on Organic-Inorganic Hybrid Nanoflower for Efficient Hydrogen Generation, Appl. Surf. Sci., 574, 151725 (DOI: 10.1016/j.apsusc.2021.151725).
- Kaushik A., Kumar R., Arya S. K., Nair M., Malhotra B. D., Bhansali S. (2015), Organic-Inorganic Hybrid Nanocomposite-Based Gas Sensors for Environmental Monitoring, Chem. Rev., 115, 4571–4606 (DOI: 10.1021/cr400659h).
- Liu J., Yang Q., Zhang L., Yang H., Gao J., Li C. (2008), Organic-Inorganic Hybrid Hollow Nanospheres with Microwindows on the Shell, Chem. Mater., 20, 4268–4275 (DOI: 10.1021/cm800192f).
- (5) Mandal B., Biswas A., Aaryashree, Sharma D. S., Bhardwaj R., Das M., Rahman M. A., Kuriakose S., Bhaskaran M., Sriram S. Than Htay M., Das A. K., Mukherjee S. (2018), π-Conjugated Amine-ZnO Nanohybrids for the Selective Detection of CO₂ Gas at Room Temperature, ACS Appl. Nano Mater., 1, 6912–6921 (DOI: 10.1021/acsanm.8b01731).
- (6) Jadhav R. G., Das A. K. (2020), Pulse Electrodeposited, Morphology Controlled Organic-Inorganic Nanohybrids as Bifunctional Electrocatalysts for Urea Oxidation, Nanoscale, 12, 23596–23606 (DOI: 10.1039/d0nr07236b).
- Manna B., Raj C. R. (2017), Inorganic-Organic Hybrid 3D Redox Nanoarchitecture for the Electrocatalytic Sensing of Thiols, ACS Sustain. Chem. Eng., 5, 9412–9422 (DOI:

10.1021/acssuschemeng.7b02523).

- (8) Pang Z., Zhu Y., Li X., Chen M., Ge M. (2019), Room Temperature Ammonia Gas Sensor Based on Polyacrylonitrile/Silver@Polyaniline Nanofibers, IEEE Sens. J., 19, 11021–11026. https://doi.org/10.1109/JSEN.2019.2935232.
- Bagchi S., Ghanshyam C. (2017), Understanding the Gas Sensing Properties of Polypyrrole Coated Tin Oxide Nanofiber Mats, J. Phys. D. Appl. Phys., 50, 105302 (DOI: 10.1088/1361-6463/aa5906).
- (10) Gao, B.; Hao, P.; Li, G. P.; Shen, J.; Fu, Y. (2021), Naphthodithiophenediimide (NDTI): Synthesis, Structure, and Applications, Dalt. Trans., 50, 13993–14000 (DOI: 10.1039/d1dt 02555d).
- (11) Bhosale S. V., Jani C. H., Langford S. J. (2008), Chemistry of Naphthalene Diimides, Chem. Soc. Rev., 37, 331–342 (DOI: 10.1039/b615857a).
- (12) Ali S., Jameel M. A., Oldham G., Gupta A., Shafiei M., Langford S. J. (2022), Enhancement in Room Temperature Ammonia Sensing Properties of Naphthalene Diimides through Core Expansion, J. Mater. Chem. C, 10, 1326–1333 (DOI: 10.1039/d1tc 05362k).
- (13) Singha N., Neogi S., Pramanik B., Das S., Dasgupta A., Ghosh R., Das D. (2019), Ultrafast, Highly Sensitive, and Selective Detection of P-Xylene at Room Temperature by Peptide-Hydrogel-Based Composite Material, ACS Appl. Polym. Mater., 1, 2267–2272 (DOI: 10.1021/acsapm.9b00594).
- (14) Abdelhameed S. A. M., Vandebroek L., De Azambuja F., Parac-Vogt T. N. (2020), Redox Activity of Ce(IV)-Substituted Polyoxometalates toward Amino Acids and Peptides, Inorg. Chem., 59, 10569–10577 (DOI: 10.1021/acs.inorgchem.0c00993).
- (15) Wang L., Dong X., Huang M., Müller A. J., Wang D. (2017), Self-Associated Polyamide Alloys with Tailored Polymorphism Transition and Lamellar Thickening for Advanced Mechanical Application, ACS Appl. Mater. Interfaces, 9, 19238–19247 (DOI:

10.1021/acsami.7b04691).

- (16) Wang Y., Zhu P., Qian C., Zhao Y., Wang L., Wang D., Dong X.
 (2021), The Brill Transition in Long-Chain Aliphatic Polyamide 1012: The Role of Hydrogen-Bonding Organization. Macromolecules, 54, 6835–6844 (DOI: 10.1021/acs.macromol. 1c01141).
- (17) Franco M. A., Conti P. P., Andre R. S., Correa D. S. (2022), A Review on Chemiresistive ZnO Gas Sensors. Sensors and Actuators Reports, 4, 100100 (DOI: 10.1016/j.snr.2022.100100).
- (18) Bhosale S. V., Bhosale S. V., Kalyankar M. B., Langford S. J. (2009), Ultrafast, Highly Sensitive, and Selective Detection of P-Xylene at Room Temperature by Peptide-Hydrogel-Based Composite Material, Org. Lett., 11, 5418–5421 (DOI: 10.1021/o 19022722).
- (19) Tang H., Li Y., Zheng C., Ye J., Hou X., Lv Y. (2007), An Ethanol Sensor Based on Cataluminescence on ZnO Nanoparticles, 72, 1593–1597 (DOI: 10.1016/j.talanta.2007.01.03 5).
- (20) Wang Z., Tian Z., Han D., Gu F. (2016), Highly Sensitive and Selective Ethanol Sensor Fabricated with In-Doped 3DOM ZnO, ACS Appl. Mater. Interfaces, 8, 5466–5474 (DOI: 10.1021/acsami.6b00339).
- (21) He C., Cheng J., Zhang X., Douthwaite M., Pattisson S., Hao Z.
 (2019), Organic–Inorganic Hybrid Nanocomposite-Based Gas Sensors for Environmental Monitoring, Chem. Rev., 119, 4471– 4568 (DOI: 10.1021/acs.chemrev.8b00408).
- (22) Itagaki Y., Mori M., Sadaoka Y. (2018), EMF Response of the YSZ Based Potentiometric Sensors in VOC Contaminated Air, Curr. Opin. Electrochem., 11, 72–77 (DOI: 10.1016/j.coelec.2018. 08.002).
- (23) McGinn C. K., Lamport Z. A., Kymissis I. (2020), Review of Gravimetric Sensing of Volatile Organic Compounds, ACS Sensors, 5, 1514–1534 (DOI: 10.1021/acssensors.0c00333).
- (24) Inomata S., Tanimoto H. (2008), Hydrothermal Synthesis of

Porous In_2O_3 nanospheres with Superiorethanol Sensing Properties, J. Am. Soc. Mass Spectrom., 19, 325–331 (DOI: 10.1016/j.jasms.2007.11.008).

- (25) Shankar P., Rayappan J. B. B. (2017), Monomer: Design of ZnO Nanostructures (Nanobush and Nanowire) and Their Room-Temperature Ethanol Vapor Sensing Signatures, ACS Appl. Mater. Interfaces, 9, 38135–38145 (DOI: 10.1021/acsami. 7b11561).
- (26) Patel C., Mandal B., Jadhav R. G., Ghosh T., Dubey M., Das A. K., Htay M. T., Atuchin V. V., Mukherjee S. (2021), S, N Co-Doped Carbon Dot-Functionalized WO₃ Nanostructures for NO₂ and H₂S Detection, ACS Appl. Nano Mater., 2, 2492–2500 (DOI: 10.1021/acsanm.1c04174).
- (27) Li X. B., Ma S. Y., Li F. M., Chen Y., Zhang Q. Q., Yang X. H., Wang C. Y., Zhu J. (2013), Porous Spheres-like ZnO Nanostructure as Sensitive Gas Sensors for Acetone Detection. Mater. Lett., 100, 119–123 (DOI: 10.1016/j.matlet.2013.02.117).
- (28) Nandi N., Gayen K., Banerjee A. (2019), Assembly of Amino Acid Containing Naphthalene Diimide-Based Molecules: The Role of Intervening Amide Groups in Self-Assembly, Gelation, Optical and Semiconducting Properties, Soft Matter, 15, 3018– 3026 (DOI: 10.1039/c8sm02460j).
- (29) Cox R., Olson G. T., Pfau M., Eshaghi N., Barcus K., Ramirez D., Fernando R., Zhang S. (2017), Solution-Based Large-Area Assembly of Coaxial Inorganic-Organic Hybrid Nanowires for Fast Ambipolar Charge Transport, ACS Appl. Mater. Interfaces, 9, 16397–16403 (DOI: 10.1021/acsami.7b01413).
- (30) Liang C., Zhang X., Wang Z., Wang W., Yang M., Dong X.
 (2020), Organic/Inorganic Nanohybrids Rejuvenate Photodynamic Cancer Therapy, J. Mater. Chem. B, 8, 4748–4763 (DOI: 10.1039/d0tb00098a).
- (31) Wang C., Yu H. Y., Miao Z., Ge D., Abdalkarim S. Y. H., Yao J.(2021), Interface Growth of PANI-ZnO Nanohybrids on a Self-Formed Grapefruit Peel Aerogel to Construct a Quick Self-

Restored Gas Sensor, ACS Sustain. Chem. Eng., 10, 6573–6583 (DOI: 10.1021/acssuschemeng.1c08195).

- (32) Wang S., Tan L., Zhang C., Hussain I., Tan B. (2015), Novel POSS-Based Organic-Inorganic Hybrid Porous Materials by Low Cost Strategies, J. Mater. Chem. A, 3, 6542–6548 (DOI: 10.1039/ c4ta06963c).
- (33) Ren Q. H., Zhang Y., Wang T., Yu W. J., Ou X., Lu H. L. (2019), Facile Synthesis and Photoluminescence Mechanism of ZnO Nanowires Decorated with Cu Nanoparticles Grown by Atomic Layer Deposition, ACS Appl. Electron. Mater., 1, 1616–1625 (DOI: 10.1021/acsaelm.9b00338).
- (34) Gao J., Wu B., Cao C., Zhan Z., Ma W., Wang X. (2021), Unraveling the Dynamic Evolution of PD Species on Pd-Loaded ZnO Nanorods for Different Hydrogen Sensing Behaviors, ACS Sustain. Chem. Eng., 9, 6370–6379 (DOI: 10.1021/acssuschemeng.1c00652).
- (35) Al-gaashani R., Radiman S., Daud A. R., Tabet N., Al-douri Y.
 (2013), Synthesis of Adenine-Modified Reduced Graphene Oxide Nanosheets, Ceram. Int., 39, 2283–2292 (DOI: 10.1016/j.ceramint.2012.08.075).
- (36) Cao H., Wu X., Yin G., Warner J. H. (2012), Synthesis of Adenine-Modified Reduced Graphene Oxide Nanosheets, Inorganic Chem., 51, 2954–2960 (DOI: 10.1021/ic2022402).
- (37) Song I., Gao Y., Rong H., Wen H., Sha Y., Zhang H., Jiang H., Liu Q. (2018), Functionalization of Graphene Oxide with Naphthalenediimide Diamine for High-Performance Cathode Materials of Lithium-Ion Batteries, Sustainable Energy Fuels, 2, 803-810 (DOI: 10.1039/c7cc04972b).
- (38) Frath D., Nguyen V. Q., Lafolet F., Martin P., Lacroix J. C. (2017), Electrografted Monolayer Based on a Naphthalene Diimide–Ruthenium Terpyridine Complex Dyad: Efficient Creation of Large-Area Molecular Junctions with High Current Densities, Chem. Commun., 53, 10997-11000 (DOI: 10.1039/C7CC04972B).

- (39) Deblase C. R., Hernµndez-burgos K., Rotter J. M., Fortman D. J., Abreu D. S., Timm R. A., Diógenes I. C. N., Kubota L. T., Abruça H. D., Dichtel W. R. (2015), Cation-Dependent Stabilization of Electrogenerated Naphthalene Diimide Dianions in Porous Polymer Thin Films and Their Application to Electrical Energy Storage, Angewandte chemie, 127, 13423–13427 (DOI: 10.1002/ange.201505289).
- (40) Bhat S. A., Das C., Maji T. K. (2018), Metallated azo-naphthalene diimide based redox-active porous organic polymer as an efficient water oxidation electrocatalyst, J. Mater. Chem. A, 6 19834– 19842 (DOI: 10.1039/C8TA06588H).
- Wang T., Lv R., Zhang P., Li C., Gong J. (2015), Au Nanoparticle Sensitized ZnO Nanopencil Arrays for Photoelectrochemical Water Splitting, Nanoscale, 7, 77–81 (DOI: 10.1039/c4nr03735a).
- Li F., Peng H., Xia D., Yang J., Yang K., Yin F., Yuan W. (2019), (42)Highly Sensitive, Selective, and Flexible NO₂ Chemiresistors Based on Multilevel Structured Three-Dimensional Reduced Graphene Oxide Fiber Scaffold Modified with Aminoanthroquinone Moieties and Ag Nanoparticles, ACS Appl. Mater. Interfaces. 11, 9309–9316 (DOI: 10.1021/acsami.8b20462).
- (43) Michalchuk A. A. L., Tumanov I. A., Konar S., Kimber S. A. J., Pulham C. R., Boldyreva E. V. (2017), Challenges of Mechanochemistry: Is In Situ Real-Time Quantitative Phase Analysis Always Reliable? A Case Study of Organic Salt Formation, Adv. Sci., 4, 1700132 (DOI: 10.1002/advs. 201700132).
- Wu M., He M., Hu Q., Wu Q., Sun G., Xie L., Zhang Z., Zhu Z., Zhou A. (2019), Ti₃C₂ MXene-Based Sensors with High Selectivity for NH3 Detection at Room Temperature, ACS Sensors, 4, 2763–2770 (DOI: 10.1021/acssensors.9b01308).
- (45) Takahashi H., Hisaoka S., Nitta T. (2002), Ethanol Oxidation Reactions Catalyzed by Water Molecules : nCH₃CH₂OH + nH₂O----CH₃CHO + H₂ + nH₂O (n = 0, 1, 2), Chemical. Physics. letters,

363, 80-86, 2002 (DOI: 10.106/S0009-2614(02)01142-9).

- (46) Haq M. U., Din S. U., Khan S., Baohui D., Xuehua C., Zhu L.
 (2021), Ultrasensitive Sensors Based on PdO@SrFe₂O₄
 Nanosphere-Modified Fibers for Real-Time Monitoring of Ethanol Gas, ACS Appl. Electron. Mater., 3, 1732–1746 (DOI: 10.1021/acsaelm.1c00035).
- (47) Mandal B., Aaryashree, Das M., Than Htay M., Mukherjee S.
 (2019), Architecture Tailoring of MoO₃ Nanostructures for Superior Ethanol Sensing Performance. Mater. Res. Bull., 109, 281–290 (DOI: 10.1016/j.materresbull.2018.09.041).
- (48) Das P., Mondal B., Mukherjee K. (2016), Hierarchical Zinc Oxide Nano-Tips and Micro-Rods: Hydrothermal Synthesis and Improved Chemi-Resistive Response towards Ethanol, RSC Adv., 6, 1408–1414 (DOI: 10.1039/c5ra23203a).
- (49) Zhang D., Sun Y., Zhang Y. (2015), Fabrication and Characterization of Layer-by-Layer Nano Self-Assembled ZnO Nanorods/Carbon Nanotube Film Sensor for Ethanol Gas Sensing Application at Room Temperature, J. Mater. Sci. Mater. Electron., 26, 7445–7451 (DOI: 10.1007/s10854-015-3378-4).
- (50) Lin Y., Deng P., Nie Y., Hu Y., Xing L., Zhang Y., Xue X.
 (2014), Room-Temperature Self-Powered Ethanol Sensing of a Pd/ZnO Nanoarray Nanogenerator Driven by Human Finger Movement, Nanoscale, 6, 4604–4610 (DOI: 10.1039/c3nr06809a).
- (51) Guo Y., Xiao Y., Zhang L., Song Y. F.(2012), Fabrication of (Calcein-ZnS) n Ordered Ultrathin Films on the Basis of Layered Double Hydroxide and Its Ethanol Sensing Behavior, Ind. Eng. Chem. Res., 51, 8966–8973 (DOI: 10.1021/ie300966t).
- (52) Nur'aini A., Oh I. (2020), Volatile Organic Compound Gas Sensors Based on Methylammonium Lead Iodide Perovskite Operating at Room Temperature, RSC Adv., 10, 12982–12987 (DOI: 10.1039/c9ra10703g).
- (53) Jiang Y., Tang N., Zhou C., Han Z., Qu H., Duan X. (2018), A Chemiresistive Sensor Array from Conductive Polymer Nanowires Fabricated by Nanoscale Soft Lithography, Nanoscale,

10, 20578–20586 (DOI: 10.1039/c8nr04198a).

- (54) Wang P., Fu Y., Yu B., Zhao Y., Xing L., Xue X. (2015), Realizing Room-Temperature Self-Powered Ethanol Sensing of ZnO Nanowire Arrays by Combining Their Piezoelectric, Photoelectric and Gas Sensing Characteristics, J. Mater. Chem. A, 3, 3529–3535 (DOI: 10.1039/c4ta06266c).
- (55) Basak S., Nanda J., Banerjee A. (2013), Assembly of Naphthalenediimide Conjugated Peptides: Aggregation Induced Changes in Fluorescence, Chem. Commun., 49, 6891–6893 (DOI: 10.1039/c3cc43538e).

Conclusions and Future Perspectives

6.1 Conclusions

The main accomplishment of this thesis is the functionalization of sensing materials to detect toxic gases at room temperature, contributing to environmental sustainability. The major results of the thesis are summarized below:

Chapter 1 provides a brief overview of the significance of gas sensors, followed by an exploration of various types of gas sensors. This chapter delves into sensing parameters and potential sensing mechanisms, with a primary focus on the functionalization of sensing materials. The sensing capabilities of small organic molecules, such as NDI, PDI, pentacene, porphyrin, benzodithiazole, etc. are briefly outlined. Furthermore, the chapter addresses the challenges associated with small organic molecules. Additionally, conjugated polymers incorporating imine bonds, triazine rings, amine groups, benzothiadiazole, etc. in their backbone are examined as sensing materials. The sensing performance of organic-inorganic hybrids, including metal oxides, carbonaceous materials, noble metals, etc., as inorganic components is also discussed. The impact of electron-withdrawing groups (EWG) or electron-donating groups (EDG) and the positions of functional groups on sensing performance, particularly when functionalized with the parent material, are explored.

Chapter 2 reports the successful formation of covalent organic polymers (COPs) decorated with amide (COPO) and thioamide (COPS) bonds, achieved through mechanochemical grinding and solution phase methods, respectively. Additionally, COPO and COPS were employed as sensing materials for the selective detection of H₂S at 25 °C. The COPO sensor demonstrated a response of 2.6 times higher, reaching 190%, to 100 ppm of H₂S with a fast response/recovery time of 20/40 s compared to COPS (response = 73%). The COPO-based sensor exhibits excellent selectivity, repeatability, complete reversibility, and long-term durability, with LOD and LOQ values of 0.75 ppb and 2.5 ppb, respectively, in ambient conditions. The proposed mechanism for the COPO and COPS sensors is based on hydrogen bonding between the sensing material and H₂S molecules, which restricts the conduction of protons on the polymer

surface. Consequently, the resistance increases for COPO and COPS in the presence of H_2S , leading to the calculated responses of both sensors. These promising results suggest a viable approach for highly sensitive and selective H_2S detection, opening up a wide range of applications for COPO in industries and environmental monitoring.

Chapter 3 presents a CP decorated with thiazole rings, named BBT and further, the backbone of BBT CP was functionalized with benzolselenadiazole ring, named BBTBSe. Both BBTBSe and BBT were thoroughly characterized using various techniques. Subsequently, BBTBSe and BBT were applied onto IDE for the selective chemodetection of SO₂ at 25 °C. The BBTBSe sensor displayed a 4.3fold enhanced response (Rg/Ra) of 199.4 to 100 ppm of SO₂, with a rapid response/recovery time of 60/70 s, in comparison to BBT (response = 45.7). Furthermore, BBTBSe sensors exhibited a linear increase in response with concentration, and LOD and LOQ values were determined as 0.23 and 0.76 ppb, respectively. The sensing performance of the BBTBSe sensor to SO₂ was proposed based on the interaction of SO₂ molecules with the surface of CPs. These impressive results present a practical approach for the highly sensitive and selective detection of SO₂ gas using the BBTBSe sensor, suggesting its potential application in industries and environmental monitoring

Chapter 4 introduces the development of imine linkage nanoporous covalent organic polymers (nCOPI), which were further reduced to amine linkage nCOP (nCOPA) Subsequently, COPI and COPA were applied to IDE for the selective chemodetection of NH₃ at 25 °C. The COPA sensor demonstrated an 18.8-fold enhanced response (Δ R/Ra) of 1700% towards 500 ppm NH₃, with a rapid response/recovery time of 60/70 s compared to COPI (response = 91%). Additionally, the response of COPA sensor linearly increased with concentration, and COPA achieved LOD and LOQ values of 0.25 ppb and 0.86 ppb, respectively. The COPA sensor exhibited remarkable selectivity against other interfering gases, along with repeatability, complete reversibility, and long-term durability at 25 °C. The higher sensitivity of the COPA sensor to NH3 is attributed to hydrogen bonding, which significantly hinders the

conduction of the COPA sensor, leading to an increase in resistance and response values was calculated. Furthermore, the large surface area of the COPA sensor is considered a contributing factor to its higher sensitivity and complete reversibility towards NH₃ molecules. These impressive results propose a practical approach for the highly sensitive and selective detection of NH₃ gas using the COPA sensor, suggesting potential applications in industries and environmental pollution monitoring.

Chapter 5 demonstrates the synthesis of NDICY-ZnO nanohybrid which was detailed using a facile single-pot hydrothermal method. Subsequently, the NDICY-ZnO nanohybrid is applied in ethanol sensing at 27 °C. The sensing experiment highlights that the NDICY-ZnO nanohybrid displayed a maximum response of 66.4% to 500 ppm ethanol, surpassing the individual responses of NDICY (17.8%) and ZnO (19.6%), and exhibited a rapid response/recovery time. Notably, the response to ethanol for NDICY-ZnO significantly increased with rising relative humidity (RH); at 75% and 97% RH, the response reaches 75% and 83%, respectively. Additionally, the NDICY-ZnO-based sensor demonstrates adequate selectivity, repeatability, and long-term durability ambient conditions. The synergistic effect of NDICY-ZnO in underscores its outstanding sensing and selective behavior towards ethanol, establishing its potential as a practical sensing material with remarkable features.

6.2 Future Perspectives

The findings presented in this thesis provide valuable perspectives on the advancement of functionalized materials designed for the detection of toxic gases and volatile organic compounds (VOCs) in ambient conditions. In addition to the mentioned focus, conjugated polymers and organic-inorganic nanohybrid materials open up new possibilities for diverse applications

In chapter 2, amide and thioamide COP have been synthesized with excellent gas-sensing properties. The incorporation of amide and thioamide bonds into the semiconducting conjugated polymer imparts

basic behavior, which facilitates acid-base interactions and catalytic reactions. As a result, these COPs, known as COPO and COPS, have potential applications in heterogeneous catalytic reactions.

In chapter 3, we have synthesized benzoselenadiazole decorated CPs for detecting SO₂ gas. Benzoselenadiazole based organic compounds also show promising biomedical applications. Thus, aromatic drugs could be easily loaded onto BBTBSe through π - π stacking interactions. The host-guest interactions within this porous CPs suggest their potential as drug carriers, expanding their use beyond conventional gas sensing applications. Therefore, the benzoselenadiazole-containing BBTBSe CP has the potential for further use in drug delivery applications.

In chapter 4, the synthesis of an imine-decorated conjugated polymer (COPI) and the subsequent reduction of imine bonds to amine groups (COPA) within the polymer. The presence of amine groups and branched polyphenylene units in COPI and COPA exhibits electrocatalytic behavior, making them suitable for various electrochemical transformations, including the hydrogen evolution reaction (HER). This opens an avenue for scientists to explore diverse structures and develop a new generation of metal-free electrocatalyst.

In chapter 5, organic-inorganic nanohybrid have been developed using simple and facile hydrothermal method with adequate sensing performance. The incorporation of tyrosinated peptide sheets in these nanohybrids exhibits inherent semiconducting behavior. The synergistic effect of the nanohybrid results in efficient charge storage sites and fast charge-transport channels. As a result, the NDICY-ZnO nanohybrid could be further employed in supercapacitors for energy storage applications.

Moreover, overcoming the complexity of detecting multicomponent mixed gases in human exhaled disease diagnosis and atmospheric gas pollutant monitoring necessitates the use of a sensor array (e-nose) that integrates multiple sensor units. This, when coupled with intelligent algorithms, serves to bolster the precision of gas detection. Furthermore, the produced conjugated polymers could be functionalized or doped with guest materials, which promotes charge transfer and improves carrier transport. The inclusion of guest materials can create synergistic effects and offer complementary benefits to the host materials, thereby augmenting the sensitivity, selectivity, and stability of the gas sensors.