Nanomaterial-based Sensing of Low-concentration NO_2 Gas: A Review

Golam Imran Hussain[1], Rashi Borgohain[2]

[1,2] Department of Electronics & Telecommunication, Assam Engineering College
Jalukbari, Guwahati- 781013, Assam, INDIA.
[1]*hussain.imran55@gmail.com**, [2]*rashi.ete@aec.ac.in*

Abstract: ***This paper highlights the recent advances and new trends in nanomaterial-based detection of NO_2 in ambient air, which is the major constituent of polluted air. The development of rapid, sensitive, and reliable gas sensing techniques is essential for the benefit of human life and health. Gas sensors are emerging as important devices in both industrial and medical applications. As a result, more and more work has been done in recent years to develop gas sensors with high selectivity, sensitivity, reproducibility, and stability. As such, various nanomaterials have been explored to improve the overall performance of gas sensors, among which, ZnO, ZnO-ZnS, and carbon dots (CDs) have received enormous attention due to their excellent performance. This paper reviews the applications of ZnO, ZnO-ZnS, and Carbon Dots (CDs) for sensing low-concentration NO_2. The synthesis methods and performance characteristics of these nanomaterials are discussed in detail. Lastly, the challenges, and perspectives on the future trends of these nanomaterial-based gas sensors are highlighted.***

Keywords: Carbon Dot; Gas Sensor; NO_2; ZnO; ZnO-ZnS.

Article history- Received: 7 July 2023 and Accepted: 8 September 2023.

1. Introduction

Air pollution has significantly increased in modern society as a result of the growth of industrialization and urbanization. Nitrogen dioxide (NO_2) is one of the most hazardous sources of air pollution that results from the combustion of fossil fuels in industry, power plants, homes for heating, and automobile engines. Particularly, exposure to ppm levels of nitrogen dioxide (NO_2) adversely worsens human health. In addition, NO_2 is one of the factors that contribute to acid rain, which has several negative consequences on the environment, including acidity of surface waters. Therefore, it is crucial to create a gas sensor for the instantaneous detection and regulation of NO_2 emissions [1-4]

Gas sensors play a vital role in many different disciplines, including public safety, environmental monitoring, medical engineering, food monitoring, pharmaceutical industries, and clinical diagnostics to name a few. Nanomaterials-based gas sensing devices were developed in response to the need for miniaturized sensors with high sensitivity, time response, selectivity, reproducibility, durability, and low cost. This is because nanomaterials naturally have high surface-to-volume ratios and chemical/physical gas adsorption capacities.

Gas sensors work on the principle of transforming the composition and concentration of various gases into electric signals through complex physical and chemical effects. The sensor, which operates according to principles of optics, conductivity, acoustics, etc., processes the incoming signal (physical, chemical, or biological). Metals (Pd, Pt, Ag, Ni), semiconductors (Si, GaAs, GaN, ZnS), ionic compounds (CaF_2, Ag_2S, Na_2CO_3), and polymers (polyether, polyurethane, and Nafion) are just a few of the materials that have been created for use in gas sensing systems. Nevertheless, these materials have several drawbacks, including poor selectivity, long-term drift, toxicity, and complicated technology. Another issue is that other gases' influence might cause problems in complex sensing circumstances [5]. However, these materials suffer from various limitations such as poor selectivity, long-term drift, poisoning, and complex technology.

Because the reaction in the system is triggered by the interaction of the gas (to be measured/identified) with an active layer that is influenced by the presence of the gas, it is of significant interest to achieve materials with a greater surface-to-volume ratio to boost the performance of sensors. Hence, nanostructured materials or nanomaterials is an approach that is of great interest to the scientific community working in gas sensing [5]

2. ZnO nanomaterials for low-concentration NO_2 gas sensing

ZnO nanomaterials have witnessed an immense exploration for gas sensors due to the wide band gap (3.37eV), large exaction binding energy (60 meV), high electron mobility, and admirable physical and chemical stability [6].

In [7], gas sensors were fabricated using multiple networked ZnO nanowires and showed substantially enhanced electrical responses to NO_2 gas at 300°C. The sensor showed a response value of 263% for 10 ppm NO_2 at 300°C.

In [8], the study investigated the influence of oxygen-vacancy-related defects on the gas-sensing properties of ZnO-nanowire gas sensors. These gas sensors were fabricated by growing ZnO nanowires between two Au catalysts. The gas-sensing performance of these sensors was then characterized, with a specific focus on their response to NO_2 gas. The gas sensors showed the highest sensitivity to NO_2 gas at an operating temperature of 225°C, suggesting this temperature is optimal for detecting NO_2 efficiently.

In [9], the researchers developed a novel gas sensor chip design that aimed to enhance the performance of gas sensors by controlling the formation of ZnO nanowires (NWs). The gas sensor chip design incorporates the use of an Au catalyst, which is selectively deposited on and between Pt electrodes of a planar-type micro gas sensor. These dendrite islands serve as nucleation sites for the growth of ZnO nanowires. The gas sensors exhibited effective detection capabilities for nitrogen dioxide (NO_2) gas at a moderate operating temperature of around 250 degrees Celsius. At a low working temperature of 150°C, the sensor required significantly longer response and recovery times of about 200 and 350 s, respectively. The response and recovery times decreased with increasing working temperature, and these values at 300°C were about 15 and 20 s, respectively.

In [10], ZnO nanowire (ZNW) arrays were grown directly on the sensing electrode using a hydrothermal route for NO_2 gas sensing. The fabrication process involved two main steps: seed layer deposition and seed growth using a hydrothermal method. The results showed that the sensor response was linearly proportional to the concentration of NO_2 in the range of 1–30 ppm. The sensor exhibited good reproducibility and selectivity for NO_2 detection. The maximum sensor response to NO_2 was achieved at an operating temperature of 250°C. At higher temperatures, the response and recovery times of the sensor decreased rapidly. The maximum sensor response of 3.3 was obtained to 5 ppm NO_2 at an operating temperature of 250°C with fast response and recovery time of 25 and 21 s, respectively.

In [11], researchers have demonstrated a facile and fast nonchemical route for fabricating a resistive-type ZnO gas sensor. The gas sensor was constructed using vertically aligned ZnO Nanorod arrays grown on a Pt-electrode patterned alumina substrate. The entire process took place under ambient conditions, making it convenient and easily reproducible. The sensor demonstrated a very low detection limit of 10 parts per billion (ppb) of NO_2 gas at an operating temperature of 250°C. This means that the sensor could detect very small amounts of NO_2 in the environment.

In [12], flower-like ZnO nanostructures were successfully synthesized using a simple hydrothermal method without the use of surfactants or organic solvents. The response time and the recovery time are about 8 s and 40 s, respectively, to 10 ppm NO_2 at an optimum operating temperature of 150°C. It can be concluded that the flower-like ZnO synthesized by a simple hydrothermal method is a promising sensing material for NO_2 sensors.

In [13], the researchers prepared ZnO nanoparticles with varying sizes from 5 to 270 nm by annealing the precursor of zinc carbonate hydroxide at different temperatures (200, 400, 600, and 800°C). The purpose was to investigate the morphology, structure, optical properties, and gas-sensing performances of these ZnO nanoparticles, particularly concerning their response to nitrogen dioxide (NO_2). Among the ZnO samples obtained, the ZnO-400 (annealed at 400°C) showed the best optical properties and the highest sensing response to NO_2. The ZnO-400 exhibited fast response and recovery times to NO_2 ($\leq$30 s and $\leq$120 s, respectively) and demonstrated high selectivity to NO_2.

In [14], the researchers investigated the influence of ZnO nanoseeds on the formation of ZnO nanorods from ε-$Zn(OH)_2$ in a NaOH solution at 80 °C. The experimental results indicated that the presence of ZnO nanoparticles which act as seeds, promoted the rapid heterogeneous formation of ultrathin ZnO nanorods (with a diameter of 10–15 nm). The ultrathin ZnO nanorods were found to be more sensitive in detecting nitrogen dioxide (NO_2) gas at room temperature. The increased sensitivity was attributed to their higher variation of channel conduction with respect to the diameter of the nanorods.

3. ZnO/ZnS Core-Shell nanostructure for low-concentration NO_2 sensing

Single semiconductor oxides usually exhibit low sensitivity, selectivity, and reliability, and therefore, composite nanostructures like ZnO/TiO_2, In_2O_3/SnO_2, ZnO/SnO_2, etc. have been introduced to enhance NO_2 gas sensing performance. NO_2 has been detected successfully using the above composite nanostructures but at higher operating temperatures [15]

In [15], the researchers describe the development of a sensor using a ZnO/ZnS core/shell nanostructure for detecting NO_2 gas at room temperature. The results of the experiments showed that the sensor had an impressive response to NO_2 gas at room temperature. The conductivity of the sensing material exhibited a sharp decrease when exposed to NO_2 gas. The higher the concentration of NO_2, the greater the decrease in conductivity. the sensor demonstrated a response of 1800% for a concentration of 100 parts per billion (ppb) of NO_2. Furthermore, when the concentration of NO_2 was increased to 2400 ppb, the sensor's response increased to 3000%. The fabricated ZnO/ZnS core/shell nanostructure sensor is highly sensitive to NO_2 and can detect even low concentrations of the gas with a substantial response.

In [16], the researcher describes the synthesis and characterization of SnO_2-core/ZnO-shell nanowires for detecting NO_2 gas at room temperature under ultraviolet (UV) illumination. The cores of the nanowires are made of SnO_2, and they have a primitive tetragonal structure. The shells of the nanowires are composed of ZnO and exhibit a wurtzite structure.

The paper [17] discusses the synthesis and gas-sensing properties of ZnO–SnO_2 core-shell nanowires (NWs). The structure of the ZnO–SnO_2 core-shell nanowires is described as having a ZnO core with a diameter of 50–80 nm, and a crystalline SnO_2 shell layer with a thickness of 15–20 nm. These nanowires were fabricated using a continuous two-step vapour growth method at different synthesis temperatures. Results showed that the ZnO–SnO_2 core-shell NW sensor exhibited a significant enhancement in gas response to 10 ppm NO_2 compared to ZnO nanowires. The enhancement was approximately 33 times higher when the sensor was operating at 200°C.

4. Carbon dots (CDs) for low-concentration NO_2 sensing

Carbon dots (CDs) represent a relatively new type of carbon allotrope with a 0-D structure and nanoparticle sizes < 10 nm [18]. CD-based sensors enable real-time detection of ultra-low concentrations of gas molecules. Carbon dots can be synthesized from inexpensive biomass waste like orange peel, ginkgo biloba leaves, paulownia leaves and magnolia flowers [19]. CDs have a very large surface area and therefore more active sites for molecule adsorption, and this results in high conductivity which helps in rapid charge transfer. Carbon dots have emerged as promising nanomaterials for gas sensing due to their exceptional optical and electronic properties. The surface functionalization of carbon dots allows for specific NO_2 binding sites, leading to changes in fluorescence or electrical properties upon gas exposure.

The researchers in [21] present a significant breakthrough in the field of NO_2 gas sensing using carbon dots (CDs) derived from olive solid waste (OSW) as a low-cost and environmentally friendly precursor material. The CDs-sensor demonstrated remarkable gas sensing performance, including high and selective response to sub-ppm concentrations of NO_2 at a relatively low operating temperature of 150°C. Additionally, it exhibited a low limit of detection (LOD) of 50 ppb, excellent reproducibility, and stability over repeated use and ageing.

In [22], researchers used carbon dots as dopants to modify hierarchical litchi-like In_2O_3 nanospheres. The modification was carried out through a simple and environment-friendly hydrothermal approach. The sensors based on In_2O_3/carbon dots exhibited a significantly improved gas sensing response at a relatively low working temperature of 50 °C. This work demonstrates the successful modification of In_2O_3 nanospheres using carbon dots to enhance the gas-sensing properties of the material. The use of carbon dots as dopants and their subsequent incorporation into In_2O_3 nanospheres led to improved gas sensing response and excellent selectivity, making this hybrid material a promising candidate for gas sensing applications.

A comprehensive analysis of the sensing performance of ZnO, ZnO/ZnS core-shell, and carbon dot-based NO_2 sensors is presented in Table 1. Parameters such as the structure of the material, operating temperature, concentration of NO_2, response, and response time are compared to assess the effectiveness of each nanomaterial.

Table 1: Comprehensive analysis of the sensing performance of ZnO, ZnO/ZnS core-shell, and carbon dot-based NO_2 gas sensor

Material	Structure of material	Operating temperature (^0C)	Concentration (ppm)	Response	Response Time(s)	Ref
ZnO	Nanograin Nanowire	300	0.1-10	263%	310-570	[7]
ZnO	Nanowire	225	0.5	15 (Rg/Ra)	24	[8]
ZnO	Nanowire	150-300	1	51%	200-15	[9]
ZnO	Nanowire	250	5	229.82%	25	[10]
ZnO	Nanorod	250	0.01	24%	270	[11]
ZnO	Nanorod	150	10	55%	8	[12]
ZnO	Nanoparticle	~290	40	225%	<30	[13]
ZnO	Ultrathin Nanorod	RT	1	100%	-	[14]
ZnO / ZnS	Core/Shell Nanorod	RT	0.1	1800%	-	[15]
ZnO / ZnS	Core/Shell Nanorod	RT	2.400	3000%	-	[15]
SnO_2 / ZnO	Core/Shell Nanowire	RT	1	238.73%	-	[16]
SnO_2 / ZnO	Core/Shell Nanowire	RT	5	618.51%	-	[16]
ZnO/SnO_2	Core/Shell	200	10	66.3 (Rg/Ra)	50-60	[17]
C-dots	Nanoparticle	150	0.05	140%	150	[21]
In_2O_3/ C-dot	Nanoparticle	50	0.5	130%	9.6 min	[22]

5. Challenges and Future Perspectives

Nanomaterials, including ZnO, ZnO/ZnS core-shell, and carbon dots, have shown great promise in NO_2 gas sensing and other applications. However, these materials also face certain challenges that need to be addressed for their continued advancement and successful integration into practical devices.

Many nanomaterials are susceptible to degradation over time which affects their stability and performance. Future studies will be needed to address the difficulty of long-term stability and durability of ZnO, ZnO/ZnS core-shell, and carbon dot nanomaterials under various environmental conditions.

Nanomaterial-based sensors must be reproducible to be manufactured on a large scale and used in real-world applications. The general implementation of these technologies may be hampered by the variability of material qualities and sensor performance.

High selectivity is a desired characteristic for gas sensors, but it can be difficult to achieve in situations containing many different gases. To improve the selectivity of nanomaterial-based sensors and reduce interference from other gases, further research is required.

Maintaining the performance of nanomaterial-based sensors while integrating them into real-world systems and devices is difficult for commercial applications. It is another challenge.

Nanomaterials can raise safety and toxicity concerns, particularly when they are released into the environment. It's crucial to comprehend and reduce any potential health and environmental concerns linked to these materials.

The utilization of ZnO, ZnO/ZnS core-shell, and carbon dot nanomaterials in gas sensing applications, represents a promising route for technological advancement. However, it is crucial to recognize and address the challenges that these materials face. Researchers might direct their efforts towards innovative solutions and improved tactics by accepting these problems as opportunities for development and inquiry. It will be necessary to continue working together, conduct multidisciplinary research, and take an active approach to handle problems like stability, selectivity, scalability, and safety. These nanomaterials have the potential, as the innovation journey advances, to not only revolutionize gas sensing but also considerably advance a number of other fields, advancing our knowledge of materials science and improving our quality of life.

6. Conclusion

This study presents the most recent findings on NO_2 gas detection using carbon dot, ZnO, and ZnO/ZnS core-shell nanomaterials at various working temperatures. ZnO, ZnO/ZnS core-shell, and carbon dot nanomaterials offer exciting opportunities for the development of high-performance NO_2 gas sensors. They show considerable potential for handling issues with air quality monitoring and environmental protection due to their special features and improvements in synthesis and functionalization processes. Despite substantial advancements, much more study will be required in the future to address issues of long-term stability, large response and recovery time as well as high operating temperature, issues of non-repeatability and real-world application. The future of nanomaterial-based NO_2 gas sensors holds immense potential for revolutionizing environmental monitoring, public health, and industrial safety. With ongoing research and innovation, these sensors could play a vital role in air quality monitoring challenges and improving the quality of life for communities around the world.

References

[1] Swathilakshmi and S. Anandhan, “Recent development in carbon dot-based gas sensors,” *Sens. Diagn*., vol. 1, no. 5, pp. 902–931, 2022, doi: 10.1039/D2SD00074A.

[2] S. Sawalha *et al*., “Carbon-dots conductometric sensor for high performance gas sensing,” *Carbon Trends*, vol. 5, pp. 100105, Oct. 2021, doi: 10.1016/j.cartre.2021.100105.

[3] J. Xuan *et al*., “Low-temperature operating ZnO-based NO 2 sensors: a review,” *RSC Adv.*, vol. 10, no. 65, pp. 39786–39807, 2020, doi: 10.1039/D0RA07328H.

[4] R. Borgohain, R. Das, B. Mondal, V. Yordsri, C. Thanachayanont, and S. Baruah, “ZnO/ZnS Core-Shell Nanostructures for Low-Concentration NO_2 Sensing at Room Temperature,” *IEEE Sensors J.*, vol. 18, no. 17, pp. 7203–7208, Sep. 2018, doi: 10.1109/JSEN.2018.2851196.

[5] A. Yadav and N. Sinha, “Nanomaterial-based gas sensors: A review on experimental and theoretical studies,” *Materials Express*, vol. 12, no. 1, pp. 1–33, Jan. 2022, doi: 10.1166/mex.2022.2121.

[6] S. Chaudhary, A. Umar, K. Bhasin, and S. Baskoutas, “Chemical Sensing Applications of ZnO Nanomaterials,” *Materials*, vol. 11, no. 2, pp. 287, Feb. 2018, doi: 10.3390/ma11020287.

[7] S. Park, S. An, H. Ko, C. Jin, and C. Lee, “Synthesis of Nanograined ZnO Nanowires and Their Enhanced Gas Sensing Properties,” *ACS Appl. Mater. Interfaces*, vol. 4, no. 7, pp. 3650–3656, Jul. 2012, doi: 10.1021/am300741r.

[8] M.-W. Ahn *et al*., “Gas sensing properties of defect-controlled ZnO-nanowire gas sensor,” *Applied Physics Letters*, vol. 93, no. 26, pp. 263103, Dec. 2008, doi: 10.1063/1.3046726.

[9] H. Nguyen *et al*., “Controllable growth of ZnO nanowires grown on discrete islands of Au catalyst for realization of planar-type micro gas sensors,” *Sensors and Actuators B: Chemical*, vol. 193, pp. 888–894, Mar. 2014, doi: 10.1016/j.snb.2013.11.043.

[10] X. Chen *et al*., “In-situ growth of ZnO nanowire arrays on the sensing electrode via a facile hydrothermal route for high-performance NO_2 sensor,” *Applied Surface Science*, vol. 435, pp. 1096–1104, Mar. 2018, doi: 10.1016/j.apsusc.2017.11.222.

[11] E. Oh *et al*., “High-performance NO_2 gas sensor based on ZnO nanorod grown by ultrasonic irradiation,” *Sensors and Actuators B: Chemical*, vol. 141, no. 1, pp. 239–243, Aug. 2009, doi: 10.1016/j.snb.2009.06.031.

[12] S. Bai, T. Guo, D. Li, R. Luo, A. Chen, and C. C. Liu, “Intrinsic sensing properties of the flower-like ZnO nanostructures,” *Sensors and Actuators B: Chemical*, vol. 182, pp. 747–754, Jun. 2013, doi: 10.1016/j.snb.2013.03.077.

[13] F. Fan, Y. Feng, S. Bai, J. Feng, A. Chen, and D. Li, “Synthesis and gas sensing properties to NO_2 of ZnO nanoparticles,” *Sensors and Actuators B: Chemical*, vol. 185, pp. 377–382, Aug. 2013, doi: 10.1016/j.snb.2013.05.020.

[14] Y. Xia *et al*., “Nanoseed-assisted rapid formation of ultrathin ZnO nanorods for

efficient room temperature NO_2 detection,” *Ceramics International*, vol. 42, no. 14, pp. 15876–15880, Nov. 2016, doi: 10.1016/j.ceramint.2016.07.058.

[15] R. Borgohain, R. Das, B. Mondal, V. Yordsri, C. Thanachayanont, and S. Baruah, “ZnO/ZnS Core-Shell Nanostructures for Low-Concentration NO_2 Sensing at Room Temperature,” *IEEE Sensors J.*, vol. 18, no. 17, pp. 7203–7208, Sep. 2018, doi: 10.1109/JSEN.2018.2851196.

[16] S. Park, S. An, Y. Mun, and C. Lee, “UV-Enhanced NO_2 Gas Sensing Properties of SnO 2 -Core/ZnO-Shell Nanowires at Room Temperature,” *ACS Appl. Mater. Interfaces*, vol. 5, no. 10, pp. 4285–4292, May 2013, doi: 10.1021/am400500a.

[17] I.-S. Hwang *et al.*, “Synthesis and gas sensing characteristics of highly crystalline ZnO–SnO_2 core–shell nanowires,” *Sensors and Actuators B: Chemical*, vol. 148, no. 2, pp. 595–600, Jul. 2010, doi: 10.1016/j.snb.2010.05.052.

[18] L. L. Mokoloko, R. P. Forbes, and N. J. Coville, “The Transformation of 0-D Carbon Dots into 1-, 2- and 3-D Carbon Allotropes: A Minireview,” *Nanomaterials*, vol. 12, no. 15, pp. 2515, Jul. 2022, doi: 10.3390/nano12152515.

[19] C. Wang *et al.*, “Facile synthesis of novel carbon quantum dots from biomass waste for highly sensitive detection of iron ions,” *Materials Research Bulletin*, vol. 124, pp. 110730, Apr. 2020, doi: 10.1016/j.materresbull.2019.110730.

[20] A. Prasannan and T. Imae, “One-Pot Synthesis of Fluorescent Carbon Dots from Orange Waste Peels,” *Ind. Eng. Chem. Res.*, vol. 52, no. 44, pp. 15673–15678, Nov. 2013, doi: 10.1021/ie402421s.

[21] S. Sawalha *et al.*, “Carbon-dots conductometric sensor for high performance gas sensing,” *Carbon Trends*, vol. 5, pp. 100105, Oct. 2021, doi: 10.1016/j.cartre.2021.100105.

[22] M. Cheng *et al.*, “Carbon dots decorated hierarchical litchi-like In_2O_3 nanospheres for highly sensitive and selective NO_2 detection,” *Sensors and Actuators B: Chemical*, vol. 304, pp. 127272, Feb. 2020, doi: 10.1016/j.snb.2019.127272.

Authors’ Profiles

Mr. Golam Imran Hussain received the B.E. degree from Jorhat Institute of Science and Technology, Jorhat, India, the M.Tech. degree from Tezpur University, India, in 2017. He is currently a research scholar in the Department of Electronics and Telecommunication Engineering, Assam Engineering College. His research interest is in the development of nanosensors.

Dr. Rashi Borgohain received the B.E. degree from Assam Engineering College, Guwahati, India, the M.Tech. degree from Tezpur University, India, and the Ph.D. degree from Assam Don Bosco University, India, in 2018. She is currently an Associate Professor with the Department of Electronics and Telecommunication Engineering, Assam Engineering College. Her research interest is in the development of nanomaterials for environmental sensors.