ZNO NRS IN DETECTING H_2, SO_2, ETHANOL AND NO_2 GAS: A REVIEW

Abstract

In recent decades, eradicating air pollution is a rising scientific issue, due to many destructive environmental consequences, including water pollution, global warming, climate change and acidification of ocean. This happens due to increasing demand of industries. It is essential to first identifythese toxic gases releasing from industries; when dealing with air pollution. Recently, ZnO nanorod has been widely explored to detect these gases due to high response, better selectivity, low fabricating cost and suitable performance. This review paperdiscusses the various gas sensing properties of zinc oxide nanorods based material in sensing H_2, SO_2, ethanol and NO_2 gas.

Keywords: ZnO nanorod has been widely explored to detect these gases due to high response.

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I. INTRODUCTION

As industrial demand rises, more toxic, explosive, and flammable gases such as sulphur dioxide (SO_2), carbon monoxide (CO), and others, as well as other volatile organic compounds (VOCs) like ethanol (C_2H_5OH), benzene (C_6H_6), toluene ($C_6H_5CH_3$), and others, are released into the atmosphere. All living things, including people, animals, and plants, are negatively impacted by these gases. VOCs are regarded as the most hazardous toxins that can result in environmental hazards [1–4]. Therefore, there is an urgent need for the development of exceedingly delicate technology to detect hazardous and deadly gases. The detection of these gases is greatly aided by gas sensors [5]. For this purpose, gas sensors with better sensitivity and selectivity are needed. These sensors can be fabricated using various materials like semiconductor metal oxides, vapor-sensitive polymers, and other porous, structured materials. Out of the various semiconductor metal oxides available, ZnO is frequently employed as a gas-detecting material to identify dangerous and harmful gasesdue to its outstanding physical and chemical characteristics[6]. ZnO comes under the category of n-type semiconductors and possesses a broad bandgap, strong electron mobility, and significant excitation binding energy. It is particularly beneficial because of its many qualities, which include minimal cost, simple implementation, and great reliability. As a result, it is currently a focus of research for the detection of poisonous and dangerous gases. Second, because ZnO can generate a wide range of nanostructures since it is non-amorphous (crystalline) in nature, including nanoparticles and one-, two-, and three-dimensional structures [7], photocurrent can be enhanced by utilizing these ZnO nanostructures as well as various materials after doping. This increases the detector's sensitivity. Presently, numerous techniques have been established for fabrication of ZnO nanostructures. Every synthesis method has unique advantages and built-in limitations. Surfactants are used in the majority of these synthesis methods to create ZnO nanostructures. Physical vapor techniques allow for the possibility of creating 3D hierarchical ZnO structures without the need for surfactants; however, the elimination of organics from nanostructures is a significant concern and impacts the repeatability of analysis. Recent research has focused heavily on gas sensors based on one-dimensional ZnO nanostructures because of their great sensitivity and low power requirements. Particularly ZnO nanorods (ZnO NRs) have been employed extensively for low-concentration gas detection due to their wide range of conductance variations, reactivity to both oxidative and reductive gases, and extremely sensitive and selective features. This review article provides an in-depth introduction to the processes used to create ZnO NRs, as well as to their controlled development, various topologies, modifications made to enhance sensing properties, and composites used as gas sensors.

II. GROWTH METHOD TO DEVELOP ZnONRs

1. **Thermal Evaporation Method:** In this method, a gaseous phase of titled material is allowed to form clusters and then deposited on substrate. Using sputtering, resistive heating, electron beam heating, evaporation can be attained. The widely used evaporation methods are

    - Laser Ablation technique
    - Laser Pyrolysis
    - Ionised cluster beam deposition

To prepare nanorodes of ZnO, firstly convert it into vapor form either by chemical reaction or evaporation and heated up [8]. These vapors then allowed cooling down on the substrate to produce piles of nanomaterial. Although this process is simple and easy, but carried out at extremely high temperature. Some authors reported that Zinc oxide nanorods can also be produced by oxidizing Zinc in range of 500-550 °C [9].

2. **Chemical-Vapor-Deposition (CVD):** Due to simple and easy processing, this technique is used in industry to achieve coating of single crystalline films or nanocrystalline films of different materials such as organic and inorganic materials. There are many variants of this technique such as vapor phase epitaxy (VPE), plasma enhanced CVD, matello organic CVD, atomic layer epitaxy (ALE), etc. Basically, they vary in temperature, pressure of source gas and geometrical layout. In this process, transfer of reactant gas or reactant vapors occurs towards the substrate at high temperature. Initially, this technique was used to synthesize ZnO quantum dots or thin film [10]. But later on, this is also used to develop nonorods of the titled sample using the free catalytic agent. The nanorods produced by this method are free from any type of impurities. The catalyst free MOCVD is also a potential technique for developing zinc oxide nanorods (400-500 °C) [11,12].

3. **The Chemical Method:** The reason behind advantage of this method over physical method are **a) v**ery simple and inexpensive technique **b)** Less instrumentation **c)** Low temperature i.e. less than 350˚C **d)** A variety of sizes and shapes can be obtained **e)** Materials are obtained in form of liquid but can be changed into thin films or dry powder. There are many chemical method to fabricate ZnO NRs such as aqueous-solution, hydrothermal, microemulsion sol–gel method, bio mineralization, etc. O. Brien et al. have reported a new approach to prepare ZnO NRs in which zinc acetate is used in thermal decomposition of an organic oleic acid solvent to produce ZnO NRs with a monodisperse in normal length of 40–50 nm with a diameter of 2 nm [13].

III. CHARACTERISTIC OF GAS SENSORS

A set of different parameters are required to check the efficient performance of a gas sensor. Out of many parameters, some most important parameters of gas sensors are shown in Figure which are explained below

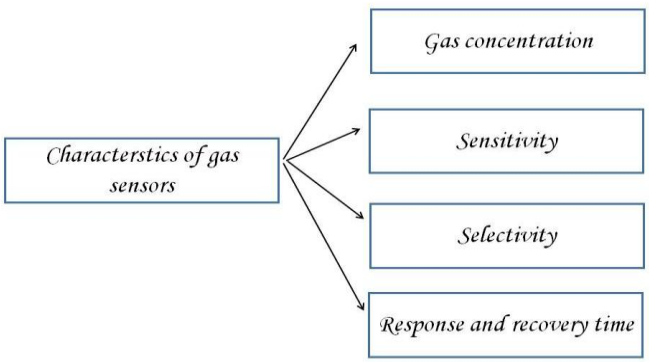

Figure 1: Different Characteristics of Gas Sensor

1. **Gas Concentration:** This is a very important factor which helps in checking the sensor performance. It will affect sensor response in terms of variation in conductivity. Generally, its unit is in ppm value or in volume percentage. The volume of the gas present in the chamber is the major factor which decides Volume percentage.

2. **Sensitivity:** Generally, background of the gas composition, humidity sensor temperature and the exposure time of film to the gas composition, all these factors greatly affect the sensitivity of the gas sensor. Sensitivity is termed as rate of change in the percentage value of thin film's resistance in the presence and absence of gas.

$$S = \frac{(R_a - R_g)}{R_a} \times 100$$

Where $R_a -$ Resistance difference of the sensing element air
$R_g -$ Air resistance for a given concentration of the gas

3. **Selectivity:** The ability by which a sensor senses a particular gas in presence of various gases is known as selectivity. Mathematically it is the ratio of sensor response towards particular gas to response towards other gases in the mixture.

$$\text{Selectivity} = \frac{\text{Sensitivity for particular gas}}{\text{Sensitivity toards other intering gas molecules.}}$$

4. **Response Time and Recovery Time:** The time taken by the sensor to attain 90% of its saturation value when exposed to test gas is termed as response time and the time when sensor recovers 90% of original resistance is known as recovery time. The value of response time varies with concentration.

IV. ZnO NRs FOR H_2 SENSING

In 2005, H. T. Wang et al. [14] developed Pd-coated ZnO-NRsutilizing sputter-depositing technology for the purpose of sensing H_2 gas at room temperature. They discovered that artificial nanostructures could detect hydrogen at concentrations as low as 10 ppm. They investigatedthat an operating voltage of 0.5 V and a sensitivity of 5% at an H_2 concentration of 500 ppm, the response and recovery periods were respectively >300 s and 20 s. They came to the conclusion that ZnO NRs are a desirable alternative for low-cost sensing applications because they can be positioned on affordable transparent substrates like glass and operate under incredibly minimal power circumstances.In 2012, C. Prakash et al. [15] hydrothermallysynthesizedZnO NRs coupled with aluminum on a glass substrate for detecting H_2. The scientists discovered that for concentrations of 150 ppm, the sensor responses of synthesized nanorods for hydrogen detection at 50, 100, and 150 °C were 10.36, 12.98, and 21.46%, respectively. At these temperatures and at the same concentration, the response and recovery periods of the nanorods produced were 76, 326 s, 45, 105 s, and 70, 204 s, respectively. They demonstrated that the presence of humidity had no impact on these parameters.In 2013, J. Hasan et al. [16] created an array of ZnO NRs on Kapton tape using the CBD process. Using XRD and SEM, the crystallinity of these rods was verified. For the purpose of detecting UV light and H_2, they created sensors from manufactured nanorods using the MSM configuration (metal-semiconductor-metal). When subjected to Ultraviolet

light at λequal to 395 nm at aoperating voltage of 30 V, the UV device showed response and decay time of 37 and 44 ms.The response and recovery periods for H_2 sensing were 400 and 187 s, respectively, at RT. They were 339 and 63 s at 150 °C and 320 and 52 s at 200 °C at concentration of 2% and sensitivity of 90% and 10%. In 2013, using the CBD approach, J. Hassan et al. [17] produced a variety of oblique and vertical ZnO NRs on the sapphire of the c-plane. They used nanocomposites of PVA-Zn $(OH)_2$ to seed the sapphire substrate before growing ZnO NRs on it. In the absence of any metal catalyst, they looked into the manufactured ZnO nanorod array's H_2 detecting capabilities. They found that these nanorods exhibit 500% sensitivity for low power consumption of less than 10 W at H_2 concentrations of 1000 ppm at RT. These nanorods were found to have response and recovery times of 176 s and 116 s, respectively, at an operating voltage of 0.1 V. In 2017, D. Sett et al. [18] prepared cobalt-doped zinc oxide nanorods (Co:ZnO NRs) for detecting H_2 gas using hydrothermal techniques. They discovered that synthesized nanorods with 8% cobalt displayed the strongest and quicker H_2 gas response ability than pure ZnO NRs at 150 °C. The response time of these nanorods was 80 sec. Recovery time was also reduced to half as compared to pure ZnO NRs.In 2018, galvanically assisted chemically generated ZnO NRs on an Au (gold)-coated Si (111) substrate were described by T. F. Choo et al. [19] for use in hydrogen sensing. They found that the performance of the sensor and hydrogen sensing behavior were significantly influenced by the applied bias voltage. Massive bias voltages can significantly lengthen response, recovery, and sensitivity times. They looked at the response and recovery times for H2 gas at 2000 ppm concentration at various voltages of -2 V, -4 V, and -6 V, which were >300, >300s; 98, 96s, and 60, 49 sec, respectively.In 2020, V. Dhingra et al. [20] studied graphene oxide (GO) and ZnO NR composites (GO-ZnO-NR) hydrothermally produced for the detection of SO_2 and H_2 gases. SEM, XRD, and Raman spectroscopy were used to undertake morphological and structural studies. At ambient temperature, the sensitivity of the synthesized composite was 5.45 for SO_2 and 5.82 for H_2 at 100 ppm. They investigated that response and recovery time for SO_2 gas was 80 and 75 s respectively and for H_2 was 30 and 40 s respectively.The comparative study of various parameters of reported sensors for H_2 gas is displayed in Table 1.

V. ZnO NRs FOR SO_2 SENSING

In 2008, Chia-Ming et al. [21] created zinc oxide nanoparticles and nanorods of different sizes using simple fabrication techniques. They used these nanomaterials to learn more about the adsorption of SO_2 and discovered that the size and shape of so-formed ZnO nanoparticles affect SO_2 adsorption. Volumetric tests revealed that bigger ZnO nanoparticles of the same shape often have an enhanced ability for poorly adsorbed SO_2 per surface area. In comparison to ZnO nanoparticles, nanorods were found to adsorb a greater amount of SO_2 per unit surface area. Different sulphur species were found to form upon heating these samples. The amounts of these species were found to be size-independent for the nanomaterials.In 2022, Brian Yuliarto et al. [22] fabricated ZnO thin film nanorod sensors using $Zn(NO_3)_2{\cdot}4H_2O$ as a precursor for detecting SO2 gases via the CBD technique by varying deposition time. To investigate how deposition time impacts gas sensing behaviour, the CBD approach was applied three times. They demonstrated that ZnO thin films with double CBD show improved sensing responses for sulphur dioxide gas at concentrations of 70 ppm at 300 °C by 15% over ZnO thin films with single CBD. The response and recovery times for nanorods having CBD carried out once were 6 and 10.8 minutes, respectively, while for twice-done CBD, these were 5.8 and 4.6 minutes. By varying operational temperatures,

the responsiveness of a twice-used CBD ZnO nanorod is 20–40% better than a once-used CBD ZnO nanorod. The unstructured, dense nanostructure of the triple CBD ZnO nanorod was less resistive and hence produced little effect on sensor performance.

VI. ZnO NRs FOR ETHANOL SENSING

In 2012, L. Wang et al. reported the creation of zinc oxide nanorods using a simple low-temperature hydrothermal process. Further its structural elucidation and surface morphology studies were done by XRD, Scanning electron microscope (SEM) and Transmission electron microscope (TEM). Further, the ethanol gas sensor was fabricated using ZnO NRs and studied its response at different operating temperatures. They have reported the response and recovery time for ethanol detection at various concentrations for different temperatures and found 6 sec and 95 sec respectively at 500 ppm for 260℃ [23]. In 2013, S. Roy developed NRs of zinc oxide for the detection of ethanol gas sensing. They discussed the effect of Pd-Ag on the ethanol sensing properties of zinc oxide nanorods. They concluded that the Pd@ZnO NRs sensor exhibited 14 and 70 sec response time and recovery time respectively towards gas concentration 1530 ppm at 200℃ [24]. In 2019, P. Cao et al. prepared vertically aligned ZnO NRs (ZnO-NRs) using CVD technique on silicon substrate and precise decoration of its surface was done using palladium nanoparticles through RF magnetic sputtering. They have studied the effect of composition of Pd-NPs on the various properties of pure ZnO-NRs such as structure, morphology of surface, gas sensing properties and elemental composition. They have concluded that Pd-NPs loaded zinc oxide structures showed four times better gas response than pure ZnO-NRs which is due to catalyticity of palladium nanoparticles. Such a high response in ethanol gas sensing is mainly due to the catalyticity of Pd-NPs [25]. In 2019, Y.C. Liang synthesized nanorods of ZnO–WO_3 using a combined method of hydrothermal growth and sputtering. Later on, modification in the structure of composite nanorods was achieved through a thermal annealing process in an atmosphere that contained hydrogen at 400℃. The annealing process increased the gas detecting properties of pristine ZnO–WO_3 nanorods. The composite nanorod which was annealed at 400℃ showed a response of 16.2 sec whereas at pristine ZnO–WO_3 showed a response of 7.3 at 50 ppm gas concentration [26]. In 2023, H.R. Madvar prepared pure and CuO-decorated zinc oxide nanorods for detection of ethanol gas with variable thickness 5,10 and 20 nm Cu layer. Its formation and surface morphology were studied using XRD, SEM, and EDS. From the experiments, it was concluded that the sensor fabricated with a 5 nm thick layer of initial Cu exhibited the highest response towards ethanol gas. Its response time was found to be 53.4 for ethanol concentration 50 ppm at 350 ℃. In addition to that, the response time and recovery time was found to be 2.2 and 166 s for 100 ppm concentration [27].

VII. ZnO NRs FOR NO_2 SENSING

Using thermal evaporation method, Navale et al reported the preparation of NWs and NRs of ZnO for NO_2 gas sensing. They observed sensing response were 101 and 612 for NO_2 gas having concentration 100 ppm at an operating temperature of 200℃ for prepared ZnO NWs and NRs respectively. Further its response and recovery time was also calculated and found to be 17 s and 290 s for nano wires and 35 s and 206 s for nanorods[28]. Thermal evaporation and solvothermal methods were employed by G.J. Sun et al in 2017 to prepare pristine and CaO-decorated ZnO NRs. By decorating the surface of zinc oxide with Cao, enhanced properties of NO_2 gas sensing s compared to pristine were observed. This is due to

the large surface area of CaO Decorated zinc oxide nanorods, large ratio of surface area and volume. Moreover, this sensor demonstrates excellent selectivity toward NO_2, CO, ethanol. The author observed response and recovery time is nearly 110 and 111 sec. for 200 ppm of NO_2 at 200℃ while pristine ZnO NRs showed nearly 121 and 122 sec at the same parameters. [29] The surface of zinc oxide nanorod was decorated by Au and Pd which was reported by E. Dilonardo in 2007. A further prepared sample was annealed at 330 and 550 °C. A rod like structure was observed at operating temperature 550℃ and observed better selectivity and response time towards NO_2 gas detection as compared to pristine. The response time and recovery time was measured for different concentrations of NO_2 gas. On the other hand, spherical structure was obtained for the sample annealed at 300 ℃ and observed worst results of sensor response towards NO_2 [30].

Table 1: Comparative Study of Various Parameters of ZnO NRs Based Sensors for Detection of Various Gases.

Material	**Gas Detected**	**Con/ ppm**	**Operating Temperature °C**	**Response Time(s)**	**Recovery Time(s)**	**Ref.**
Pd-coated ZnO NRs	H_2	500	RT	>300	20	[14]
Al coupled-ZnO NRs	H_2	150	150	70	204	[15]
ZnO-NRs	H_2	200	RT	320	52	[16]
ZnO-NRs	H_2	1000	RT	176	116	[17]
Co:ZnO NRs	H_2	3000	150	80	…	[18]
Au-Si/ ZnO-NRs	H_2	2000	RT	60	49	[19]
GO-ZnO-NR	H_2	100	RT	30	40	[20]
GO-ZnO-NR)	SO_2	100	RT	80	75	[20]
ZnO-NRs	Ethanol	200	320	54	61	[23]
Pd decorated @ZnO-NRs	Ethanol	500	260	6	95	[24]
Pd modified ZnO NRs	Ethanol	200	1530	14	70	[25]

ZnO/WO_3	Ethanol	50	300	16.2		[26]
CuO-decorated ZnO NRs	Ethanol	50 100	350 350	53.4 2.2	- 166	[27]
ZnO-NRs	NO_2	100	200	35	206	[28]
Au@ZnO	NO_2	10	550	240 ± 20	654 ± 20	[29]
CaOdecorated ZnO NRs	NO_2	200	300	110	111	[30]

VIII. CONCLUSION AND FUTURE PROSPECTIVE

ZnO NRs for gas sensors were discussed in this article. By using several production techniques, ZnO NRs of varied morphologies were created. Their synthesis procedures, and descriptions of the sensing parameters including response times, selectivity and strong stability etc.were also incorporated. Additionally, by adjusting the reaction settings, the growth of ZnO NRs can be optimized.The improvement of the sensing properties of the ZnO NRs was described from a microscopic perspective. The ZnO NRs can form various unique forms. Doping with different metals and decorating with CaO or Pd can all significantly boost the sensing performance.Future prospects for sensors based on ZnO NRs include novel production techniques, more improvement, and more composites with different doping. For the actual implementation, the sensing qualities such as accountability and stability need to be increased. The ZnO nanorod sensors' detecting method is also undefined and has to be more precise. In conclusion, significant advancements have been needed in the study of ZnO NRs for gas sensing applications.

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