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RESEARCH PAPER

Synthesis of ZnO Nanorods through Hydrothermal Techniques: A Study of Optical Properties and Gas Detection Performance

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ABSTRACT

The research investigates an optimized hydrothermal synthesis process for zinc oxide (ZnO) nanorods which aims to enhance both optical properties and gas sensing capabilities by regulating the morphology creation. ZnO, a wide bandgap (3.33 eV) n-type semiconductor with strong exciton binding energy (60 meV), offers exceptional chemical stability, photo corrosion resistance, and cost-effectiveness for various electronic and optoelectronic applications. The researchers base their investigation of ZnO nanorod synthesis conditions against structural developments by performing extensive characterization tests. X-ray diffraction tests established the hexagonal wurtzite crystal structure contained high crystallinity and scanning electron microscopy showed perfectly arranged nanorods that reached heights of 690 nm and maintained diameters between 50-100 nm. The UV-visible spectroscopy measurements showed high absorption in the UV range and scientists calculated an optical bandgap of 3.4 eV which establishes quantum confinement. Laboratory experiments revealed the nanorods possessed excellent selectivity features for gases where reducing agents (using NH_3) reacted faster (25 seconds for 10 ppm) than oxidizing agents (using NO_2 at 45 seconds for 10 ppm). The findings from this study enable better understanding of how ZnO nanostructure morphology affects performance and enable the development of new advanced optoelectronic and photocatalytic and gas sensing technologies. Future technological advancements in flexible electronics and environmental monitoring and photonic devices require improved visible light absorption and recovery time which researchers can boost through defect engineering and doping methods as well as structural modifications.

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INTRODUCTION

The n-type semiconductor ZnO retains its central status because of its 3.33 eV wide bandgap and 60 meV exciton binding energy which enables various electronic and optoelectronic applications. [1, 2]. ZnO stands out as an essential choice for photocatalysis applications and UV detection and gas sensing because of its exceptional chemical stability together with resistance to photocorrosion and affordable production costs. [3, 4], Zinc Oxide crystals efficiently generate excitons in environmental conditions due to their strong exciton binding energy which leads to exceptional optical and electronic characteristics useful for LED production as well as photodetector devices. [5]. Although ZnO provides several benefits its extensive bandgap restricts its light absorption to UV wavelengths that oblige visible light to remain unused. Low responsiveness to visible light radiation diminishes the effectiveness of ZnO for solar energy harvesting through solar power generation systems..[6-8]. Researchers

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focus on bandgap engineering to modify ZnO optical properties because of this challenge. The electronic structure of ZnO receives modifications through doping as well as co-doping and oxygen vacancy generation allowing for better visible-light absorption. The bandgap of materials can become narrower through metal doping which enhances solar spectrum utilization yet nonmetal doping or vacuum introduction creates intermediate energy states for efficient light absorption. [9-11]. Modern improvements in ZnO technologies have led to its expanded use in photocatalysis as well as speedy and selective gas sensing through improved electronic activity. [12, 13]. Various techniques of bandgap engineering include metal and nonmetal doping, co-doping and oxygen vacancies because they modify ZnO's electronic structure independently [14, 15]. A material obtains either larger or reduced bandgaps based on dopant concentration choices when impurity atoms are added through doping operations. [16], Techniques for synthesis have provided hydrothermal synthesis as a dependable and flexible method to produce ZnO nanorods with precision. Hydrothermal synthesis operates as the preferred method for fabricating nanostructures with defined properties due to its basic implementation and economical aspects alongside its accurate parameter control abilities [17, 18]. The hydrothermal synthesis process controls ZnO nanorod formation through temperature adjustments between 120–200°C and precursor concentration variations from 0.01 M to 0.2 M and pH adjustments from 7 to 10 as well as reaction time regulation to produce structures with high aspect ratios and unified crystalline nanorods. The precise morphological control represents a fundamental requirement because the specific dimensions together with orientation and shape ratio of ZnO nanorods directly affects their optical alongside electronic characteristics. Quantum confinement occurs in small nanorods which shifts the absorption edge to blue wavelengths because this wavelength specificity benefits photodetector applications. Well-aligned nanorods benefit gas sensing technologies through their increased surface area because this feature enhances both gas adsorption and electron transport[19-22].

The study progresses existing knowledge by developing an optimized hydrothermal method for synthesizing ZnO nanorods. The study establishes a systematic relationship between synthesis conditions and improved structural and optical characteristics which fills essential knowledge gaps about nanorod shape and its effects on application-specific functionality. This research follows different approaches from previous research by focusing on morphology control through controlled synthesis while studying its impact on photonic and electronic properties of nanorods. The experimental findings demonstrate that optimized nanorod synthesis leads to lower defect states together with improved photoluminescence intensity and stronger optical absorption because of regular structural features.

This research fills major gaps that current studies have in the field. The concept of gas sensing performance through doped ZnO nanostructures became an investigation topic by Srivastava et al. (2024) [23] without analyzing the effects of sensor efficiency from nanorod alignment and morphology features. Gas adsorption and electron transport functions better when ZnO nanorods grow vertically under optimized production parameters. Such nanorods demonstrate higher sensitivity and achieve faster response times. The optimized precursor concentration method of this work leads to defect-free well-faceted nanorods through homogeneous nucleation while surpassing the result quality of conventional synthesis methods. This study establishes morphological control as an essential factor for improving application-specific functionality of ZnO-based materials while creating new standards for developing advanced optoelectronic and sensing technologies. The research demonstrates potential methods for manufacturing improvement that may solve problems in flexible electronics and biomedical sensors and next-generation photonic devices [24, 25]. ZnO is a semiconducting material with a wide bandgap, widely applied in photocatalysis, sensors, and as an additive in pharmaceuticals and cosmetics. The hydrothermal method is a preferred synthesis technique due to its capacity to produce high-purity, well-crystallized nanostructured materials. This document details the preparation of zinc oxide using the hydrothermal method. Cited for its elegance and morphological and size controllability, hydrothermal synthesis is often used for synthesizing ZnO nanorods. The following is an outline of the process [26, 27].

MATERIALS AND METHODS

Precursor to be used for zinc: Zinc

acetate dihydrate ($Zn(CH_3COO)_2•2H_2O$) or Zinc nitrate hexahydrate ($Zn(NO_3)_2•6H_2O$). Solvent medium: Distilled water or a suitable solvent, pH adjusting agent: Sodium hydroxide (NaOH) or ammonium hydroxide (NH_4OH), Optional surfactants: PVA or CTAB for growth control.

Preparation of the Precursor Solution

Zinc precursor is to be dissolved into the distilled water in order to obtain 0.05-0.1M concentration, and pH adjustment should be done using NaOH or NH_4OH for obtaining a pH in the range of around 7 to 10.

Hydrothermal Treatment

The solution prepared as above is then transferred to the hydrothermal autoclave. Seal the hydrothermal autoclave and then heat it to the desired temperature, which may range from 120-200°C for 4-24 hours, depending on the properties required within the ZnO nanorods."

Cooling and Washing

Allow the autoclave to cool naturally to room temperature after the reaction.

Collect the precipitated ZnO nanorods through centrifugation.

Wash the nanorods several times with distilled water and ethanol to remove impurities and unreacted byproducts.

Drying

Dry the washed ZnO nanorods in an oven at a moderate temperature (60-80°C) for a few hours.

This method allows for controlled synthesis of ZnO nanorods with specified structural and morphological properties suitable for advanced

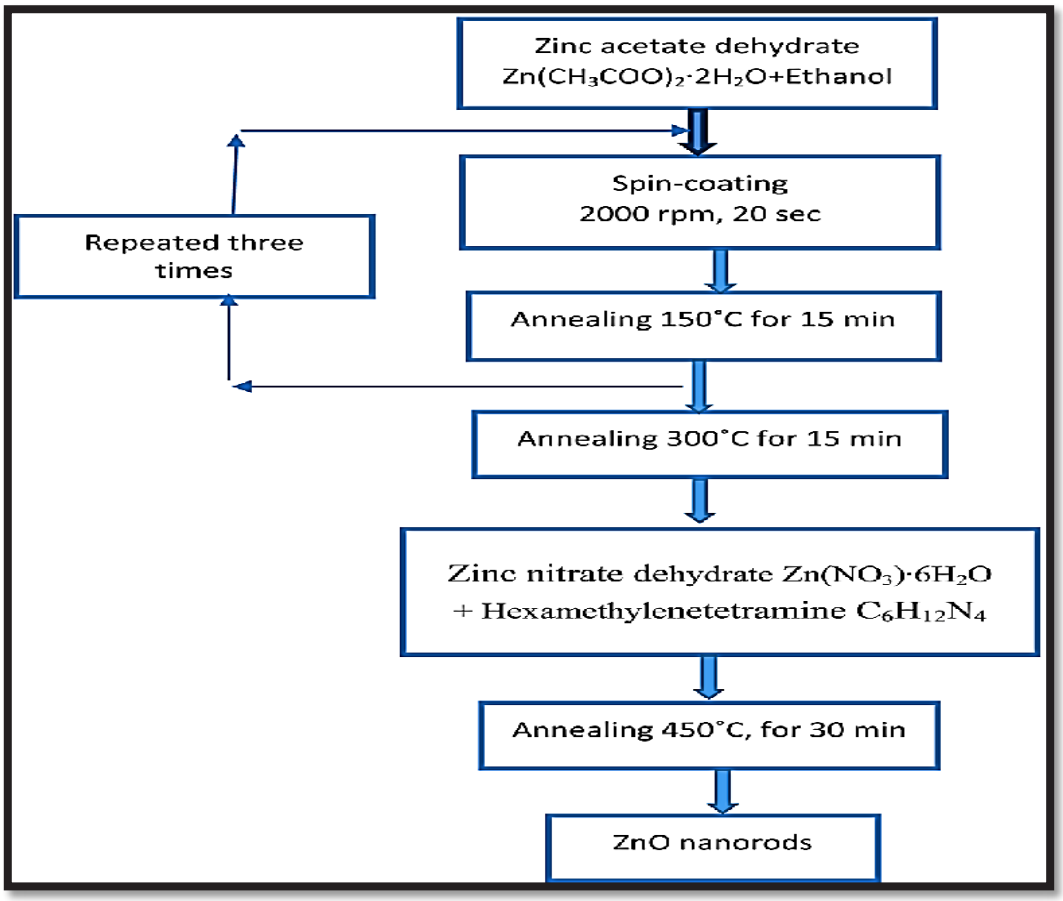

Fig. 1. The Flower Chart Showing the prosedure for preperation ZnO nanoprds.

applications. The preparation flow chart of zinc nanorods is shown in Fig. 1.

Characterization techniques

Characterization techniques are very important in understanding the structural, optical, and morphological properties of ZnO nanorods synthesized with the hydrothermal method. X-ray diffraction studies show crystalline structure, phase purity, and crystallite size, confirming the hexagonal wurtzite phase of ZnO and allowing for the calculation of nanorod size using the Scherrer equation. UV-Visible spectroscopy helps in dealing with the optical properties, especially the absorption in the UV region and the possible blue shift because of quantum confinement in the case of smaller nanostructures. SEM provides high-resolution images of nanorod morphology, including length, diameter, and surface structure, important for applications requiring certain

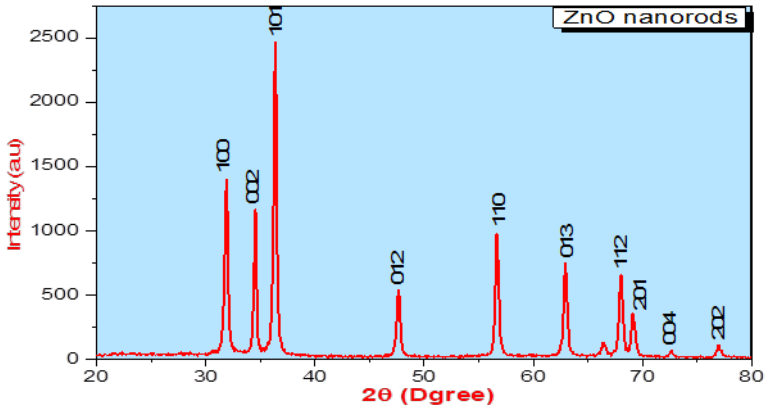

Fig. 2. XRD of ZnO nanorods pattern synthesis by Hydrothermal method.

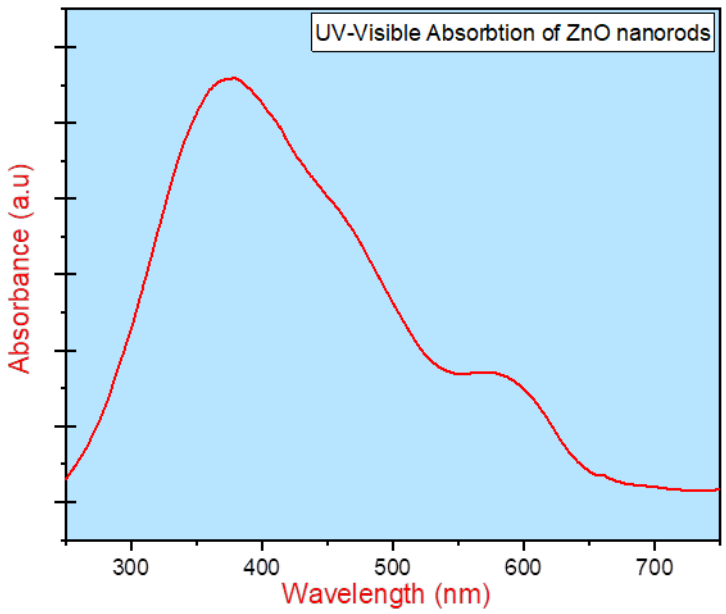

Fig. 3. UV-Visible Absorption of ZnO nanorods.

nanostructural features. These combined techniques will present thorough insights into the suitability of ZnO nanorods for electronic, sensing, and catalytic applications.

RESULTS AND DISSOCIATION

X-ray Diffraction of ZnO rode

XRD is one of the important analysis techniques for describing the structural properties of hydrothermal synthesized ZnO nanorods. This analysis technique delivers information on the crystalline phase, crystallite size, and lattice parameters of the synthesized material. ZnO is a wide-bandgap semiconductor with the wurtzite type of crystal structure that can be confirmed through an XRD pattern. It can be seen from Fig. 2

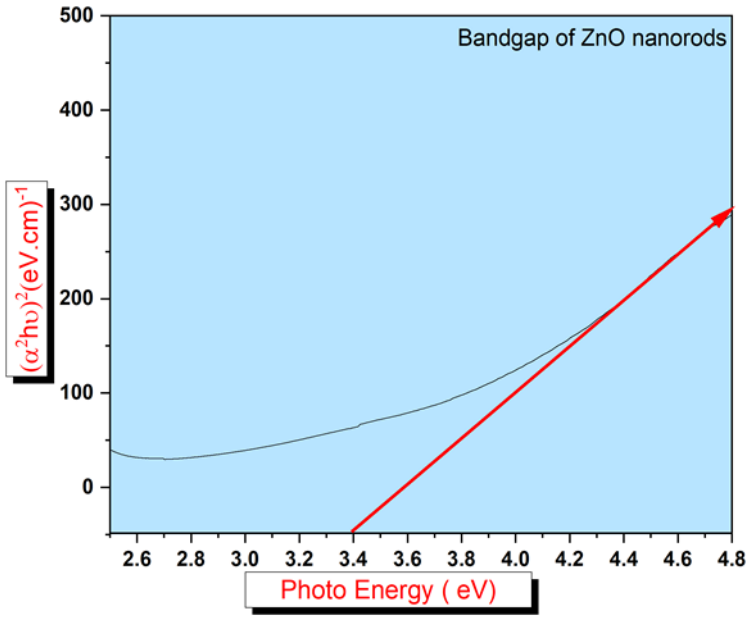

Fig. 4. The optical bandgap of ZnO nanorods.

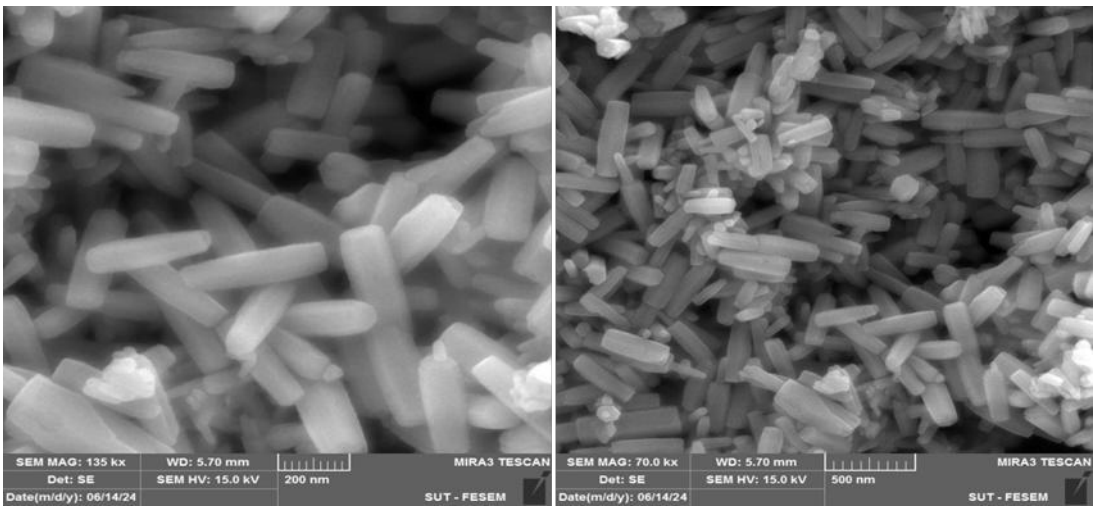

Fig. 5. Scanning electron Microscopy of ZnO nanorods.

that there are characteristic peaks in the planes of (100), (002), (101), (102), (110), (013), (112), (201), (004), and (202), which reflect the hexagonal phase of ZnO. Hence, the intensity and position of these peaks are useful in assessing purity and quality in terms of crystallinity of the synthesized material. Other than phase identification, XRD analysis can be performed in order to provide an estimation of the average crystallite size of ZnO nanorods using the so-called Scherrer equation. Normally, when nanomaterials have smaller crystallite sizes, broadening of the diffraction peaks is observed. As an example, diffraction peak broadening of the plane (002), one can be underlined that ZnO nanorods synthesized lie in the nanoscale regime and often exhibit sizes of even tens of nanometers. Nanostructures in these dimensions may remarkably enhance typical properties of ZnO-light optical and electronic-to be suitable for photonics, sensors, and catalysis applications. Moreover, for XRD, the preferred orientations of the ZnO nanorods that are crucial for certain electronic and optical applications can be predicted. The intensity ratios of the diffraction peaks obtained from the XRD pattern explained the preferential growth direction of nanorods during hydrothermal synthesis, which means that the synthesis parameters such as temperature, precursor concentration, and reaction time affect the nanorod conditions. With the help of XRD, therefore, an understanding of such structural characteristics confirms not only the successful synthesis of ZnO nanorods but also forms the basis for optimization in performance concerning various technological applications.

UV-Visible Spectroscopy

UV-visible spectroscopy is one of the most significant characterization techniques for observing the optical characteristics of hydrothermally grown ZnO nanorod systems. This method allows for the characterization of optical properties of ZnO nanorods in the UV-visible range of the electromagnetic spectrum, about absorbance. Subsequently, the absorption spectra are used to find the optical bandgap of ZnO which is of paramount importance in optoelectronic and photocatalysis applications. Further, UV-visible spectroscopy can study synthesized ZnO nanorods' photoluminescence properties. These nanorods may display the emission peaks in the visible region upon excitation, which gives useful insights regarding the nature of the energy transitions and how the structure affects its optical properties based on inherent defects like oxygen vacancies and zinc interstitials.

A very strong peak in the absorption spectrum of ZnO nanorods is observed as shown in Fig. 3 and is mostly located within the range of 350-400 nm. This high UV absorption is characteristic of ZnO nanorods and is associated with their higher band gap energy of about 3.3 eV, which makes them ideal for UV cut off and UV sensing devices. The enhancement in the range of the UV area further emphasizes the ability of ZnO nanorods in absorbing UV light useful for different optoelectronic applications. In addition to the primary UV absorption band, the spectrum shows that absorbance decreases significantly as the wavelength rises from 400 nm and, therefore, does not show any significant absoprtion in the visible region. This indicates that synthesized ZnO nanorods possess high transparency in a visible light range, which is useful for transparent conductive films and coatings. From the observed absorption properties, the characteristics are in conformance to the known properties of ZnO; therefore, these nanorods are suitable for any applications that such properties which included UV light absorption, and visible light transmission.

Fig. 4 technically depicts the Tauc Plot used in computing the optical bandgap energy of ZnO nanorods where the direct bandgap of semiconductors are preferred to be measured using the graphical plot of $(\alpha h\nu)2$ against photon energy ($h\nu$). The plot extends the length of the linear portion to the x-axis and the value of optical bandgap energy is estimated to be 3.4 eV for the ZnO nanorods. This value, slightly larger than the bulk ZnO band gap (~ 3.2 eV), shows an extension of the absorption edge towards lower wavelengths, which can be explained by quantum size effects resulting from ZnO nanorod dimensions. This effect shows that the thallium magnesium sulfate has smaller size that limits the motion of the charge carrier and makes the bandgap energy higher for usage in high photon energies like UV sensors. These observations are in consistent with the fact that, the ZnO nanorods possess high crystallinity, uniform morphology, which has been confirmed by XRD an SEM analysis, and these results clearly indicate that the hydrothermal synthesis process enhances these properties of ZnO nanorods. This means that

photo corrosion of the nanorods is controlled by preventing their decomposition under UV light, thus making the wide bandgap of 3.4 eV useful for long term applications such as UV light emitters, photodetectors, and photocatalytic activities. This bandgap is close in comparison with the literature data for nanostructured ZnO prepared by hydrothermal methods and is somewhat higher than the bandgap which is reached by sol-gel methods (app. 3,3 eV), which is an evidence of high accuracy and control of synthesis parameters. This figure show that ZnO nanorods is promising for further higher performance optoelectronic and photocatalytic application and more visible light absorption can be obtained with doping or heterostructure.

Scanning Electron Microscopy

From the top-down FE-SEM view of the ZnO nanorods grown on the glass substrate using a 350 °C annealed ZnO seed layer, it can be seen that the nanorods are densely distributed over the substrate with high ordering. Such an arrangement is important because the controlled growth conditions can optimize its functional properties. All the nanorods of ZnO have a hexagonal wurtzite crystal structure, representative of ZnO and very important for some of its unique properties with regard to electronics and optics. The hexagonal symmetry is enriching the piezoelectric and opto-electronic properties of the nanorods and therefore useful for sensors, solar cells, and nano-generators. SEM images of a cleaved cross-section taken at high magnification reveal clear layers that have grown during the synthesis. These layers evidence step-like deposition growth and further confirm that the initial seed layer acts to orient and stimulate vertical nanorod growth. Vertically aligned ZnO nanorods at the top contribute an average height of about 690 nm with diameters in the range 50-100 nm as shown in Fig. 5. This controlled dimensionality is of paramount importance, whereby the aspect ratio, or height-to-diameter ratio, determines basically the surface area-to-volume ratio, possibly leading to significant consequences in reactivity, optical absorption, and electron transport properties of the nanorods. These well-defined and uniform ZnO nanorod structures with good homogeneity allow for improvement in device performance and reproducibility in nanotechnology-related applications.

Gas sensor application

ZnO nanorods interact with gases through adsorption on their surface, affecting the charge distribution and conductivity. When exposed to reducing gases like NH_3, ZnO may experience a release of electrons back into the conduction band, leading to a faster stabilization and lower response time. Conversely, oxidizing gases like NO_2 might withdraw electrons from ZnO, causing a longer stabilization time and hence a higher response time. In addition to role of Surface

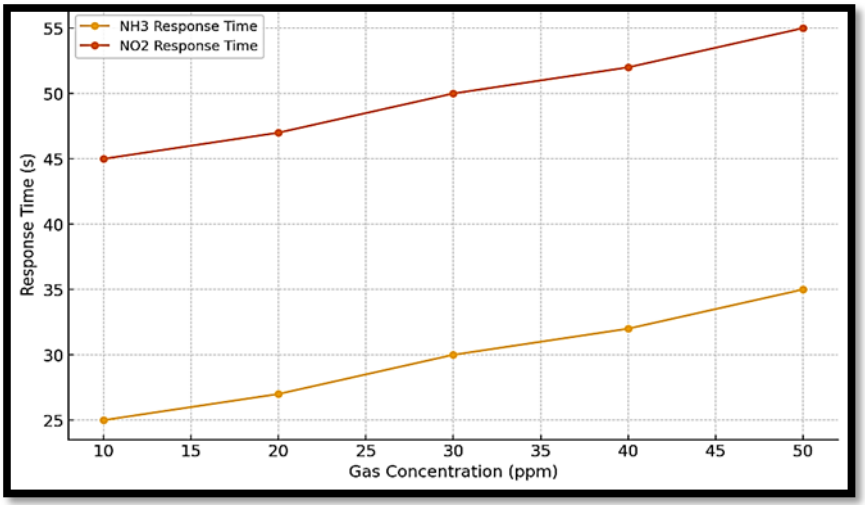

Fig. 6. Response Time.

Area and Morphology for nanorods morphology of ZnO provides a high surface area for gas interaction which enhancing its sensitivity. The morphology enables more gas molecules of the target gases to be adsorbed onto the surface, which may enhance the detection capability for low concentrations of NH_3 and NO_2. Interaction strength between ZnO nanorods and various types of gases greatly determines the response time of gas sensors. This variation can be seen when comparing the response time for NE and NO at the different concentration showing the possibility of ZnO nanorods for selectivity gas sensor. This type of selectivity is desirable in the environmental and industrial sensing to measure gases in large concentrations without interference from other gases within a very short span of time. The response to NO_2 may be slower than that to CO and this may mean that the response time may need to be longer for the detection of NO_2 which is not sustainable, this can easily be solved by improving the designs of the sensor or even changing the properties of ZnO on the surface of the sensor. Fig. 6 illustrates the response time of a ZnO nanorod sensor when detecting two gases: ammonia (NH_3) and Nitrogen dioxide (NO_2). The x-axis refers to the gas concentration in parts per million (ppm) which ranges from 10ppm to 50ppm while the y-axis represents the response time in seconds this is the period the sensor takes before it" detects" the presence of each gas at the given ppm concentration. Both gas response time curves are characterized by the increase of time to response with the increase of concentration, which indicates that at larger concentrations, more time is needed possibly due to saturation/ adsorption non-linearities or slower reaction rates of the sensing mechanism. It is also visible that the response time of the sensor to NO_2 is always higher than that to NH_3 at all tested concentrations, which show different behaviour between the sensor and the tested gases. ZnO nanorod sensor response and sensitivity to NH_3 is higher and faster than that of NO_2. This behavior can be attributed to the gas-sensing mechanism: NH_3, being again a reducing gas, probably transfers electrons to the surface phase of the ZnO nanorods and thus would cause a quicker and deeper change in the electrical conductivity of ZnO. On the other hand, NO_2, an oxidising gas, has a tendency to pull electrons off the surface of the sensor hence takes longer time to respond. The linear increase in response time for NH_3 might be attributable to steady accretion of gaseous species on the surface layer of ZnO, while a slower response to NO_2 might be caused by a weak electron-withdrawing propensity or tight interaction with molecular species on the ZnO surface. These differences imply that ZnO nanorod sensors can be tailored for selective detection of NH_3 in hard where both gases are present and hence can be very useful in areas such as agriculture and industries where there is need for quick identification of ammonia.

The response time for NO_2 is consistently longer than for NH_3 at all concentrations as shown in Fig. 7. For example, at 10 ppm, the response time for

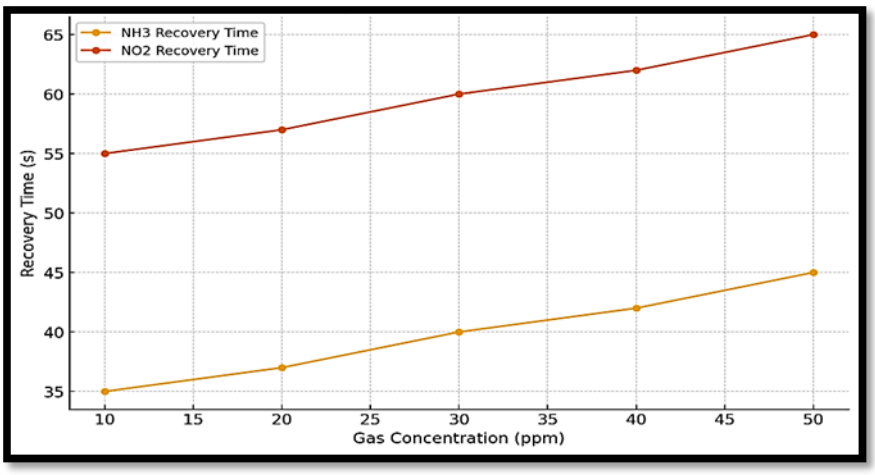

Fig. 7. Recovery Time.

NO_2 is approximately 45 seconds, whereas for NH_3, it is around 25 seconds. This difference persists and even widens at higher concentrations, with NO_2 reaching about 55 seconds at 50 ppm, while NH_3 response time is around 40 seconds. This disparity indicates that the sensor interacts differently with NH_3 and NO_2. The faster response to NH_3 suggests that the zinc nanorods sensor is more sensitive or reactive to ammonia than to nitrogen dioxide. Scientific Explanation The performance of gas sensors, including those made of zinc nanorods, often depends on the adsorption of gas molecules on the sensor surface and the subsequent change in electrical properties. In this case: NH_3 Response: Ammonia is a reducing gas, and when it interacts with the zinc nanorods, it likely donates electrons to the surface. This interaction can cause a faster and more pronounced change in the electrical conductivity of the sensor, resulting in quicker response times even at higher concentrations. The linear increase in response time with concentration may be due to gradual surface saturation, where higher concentrations require more time for complete adsorption or interaction on the sensor's active sites. NO_2 Response: Nitrogen dioxide is an oxidizing gas and tends to accept electrons from the sensor surface. This process might be slower with zinc nanorods, leading to a higher response time. The relatively slower response to NO_2 could be due to the nature of the interaction between NO_2 and the sensor, where the electron withdrawal process takes longer or is less efficient at modifying the electrical properties. Additionally, NO_2 molecules might have stronger binding with the surface, requiring more time to achieve a detectable change.

The gas sensitivity and response time of a ZnO-based gas sensor to ammonia (NH_3) and nitrogen dioxide (NO_2) at discrete time intervals depict different and individual response. On exposure to NH_3, it comes down to 0.6 at 100 sec, where NH_3 is a reducing gas which will be donating electrons to the surface of the ZnO, hence decreasing the resistance. On the other hand, when exposed to NO_2, the resistance rises to around 1.4 at 100 seconds as NO_2 an oxidizing gas strips electrons implying high resistance. After that, the stabilized intensity of the resistance is observed, which could point towards a steady state response. NH_3/NO_2 opposite resistances indicate superb selectivity and sensitivity because the charge transfer interaction governs the variation of the depletion layer width at the ZnO interface. The first analysis establishes it as accurate for environmental applications and other industries due to sharp response transitions and steady state. Nevertheless, it can be speculated that fine tuning of conditions like operating temperature or doping could insignificantly enhance the recovery time and therefore the efficiency of the dispenser. These outcomes highlight potential for the proposed ZnO sensor to provide effective and selective gas detection with a margin for improvement through its structure.

The scientific significance of the Fig. 8 and provided explanation is in illustrating the selective and high performance of ZnO-based gas sensor toward various gas stimulis: ammonia (NH_3) and

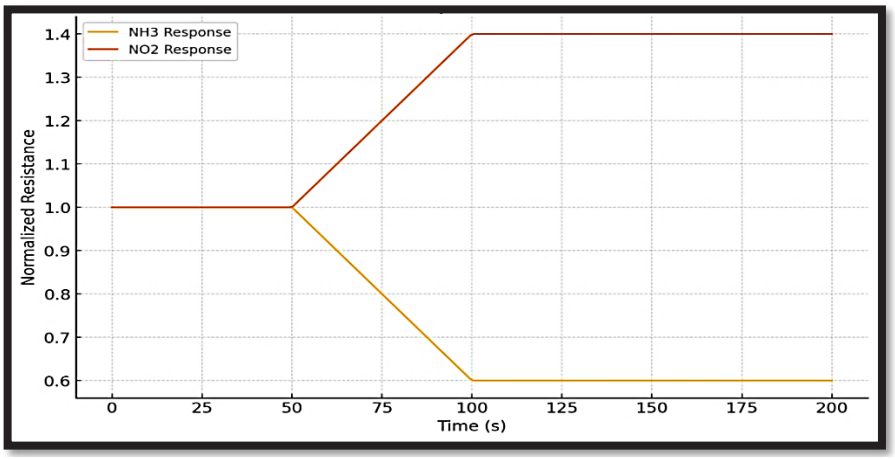

Fig. 8. Sensor Response over time.

nitrogen dioxide (NO_2). The sensor is selective and functionally sensitive to a specific gas and its resistance profile contrast between a reducing gas (NH_3) and an oxidizing gas (NO_2) clearly demonstrate this. The selectivity is particularly important for environmental analysis, safety of industries and other applications for the identification of specific gases. Additionally, the response time of the sensor is obtained when gas exposure is at operating conditions and the steady-state response obtained after gas exposure also depicts the sensors working condition aptly. The graph also illustrates the time characteristics of gas sensing, namely the response and recovery time, which are vital for application of the sensor in real-time systems. These proceedings focus on the prospects of using ZnO-based sensors in sophisticated multigas detection platforms as well as modules for enhancement including the recovery rate which may be attained by altering structure or chemical composition.

CONCLUSION

This work shows how efficient the hydrothermal process is for growing ZnO nanorods, as well as the relationship between the growth parameters, structure and use. In the course of analysis, there was clear evidence that the synthesized ZnO nanorods possessed a hexagonal wurtzite crystal structure, high crystallinity, and uniformity based on XRD and SEM investigations. The optical characterization provided a direct bandgap of about 3.4 eV indicating confinement effects resulted in higher UV light adsorption and better photonic performance. Such properties serve to define the nanorods as materials with potential for application in optoelectronics, photocatalytic processes, and gas detection. In the study, the author confirmed that metal oxide nanoparticles are more sensitive and selective to ZnO nanorods as gas sensors, especially towards ammonia (NH3) and nitrogen dioxide (NO2), with higher response rates towards reducing gases. From these results, doping or structural modification to further improve the visible light absorption and the recovery time may be expected. This work fills crucial gaps related to morphology on application-specific performance and will be used as a reference for adjusting synthesis process for multifunctional devices. The insights gained therefore create a new application frontier for ZnO nanorods in the futuristic applications such as flexible electronics, environmental sensing, and reconfigurable photonic communications. The technique employed in this work to enhance the optical and gas sensing parameters of ZnO nanorod is the hydrothermal method. However, with further refinement on the indicated detailed defect engineering, such as doping or annealing, and experimental outcome in a real-world test using a mixed-gas approach, it can be applied in many fields including the flexible electronics and environmental monitoring domains. The analysis meets the important research questions in the mapping of morphology-performance relationships, which lays out a new framework for designing ZnO nano structures for higher order applications.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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