

Parametric and Predictive Analysis of Nanostructure Growth and Nanosensor Development for Hydrogen Detection

This chapter explores the intricate relationship between the controlled growth of nanostructures and the development of high-sensitivity nanosensor, with a particular focus on hydrogen (H_2) detection. Hydrogen, as a clean energy source, plays a critical role in the transition towards sustainable energy systems. However, its high flammability and the challenges in detecting low concentrations make efficient sensor development vital for safety and monitoring in industrial and environmental applications.

2.1 FLEXIBLE ZINC OXIDE NANOWIRE PLATFORM BY METAL-SEEDED CHEMICAL BATH DEPOSITION

This work focuses on understanding the underlying growth mechanisms and achieving controlled growth of zinc oxide (ZnO) nanowires (NWs) on metal seeded flexible substrates. Furthermore, a parametric analysis is carried out to elucidate the correlation among different growth conditions in the chemical bath deposition (CBD) technique. Through a meticulously planned experimental design, the study investigates the influence of different growth conditions on synthesis outcomes. Further, an advanced machine learning (ML) model is developed to predict the growth of ZnO NWs. Additionally, this method provides an invaluable insight into the complex relationships between growth parameters and NWs characteristics, allowing for the efficient and controlled synthesis of NWs with tailored properties.

2.1.1 Introduction

One-dimensional (1D) nanostructures are gaining popularity due to their enormous potential use in microelectromechanical and microsystem technologies. At an ambient temperature, ZnO exhibits unique properties in these nanostructured materials, such as a wide bandgap of 3.37 eV and a high excitation binding energy of 60 meV (Borysiewicz, 2019; Ong et al., 2018). Due to their large surface area to volume ratio, exceptional sensitivity to adsorbed molecules and superior electric transport properties, ZnO is highly desirable for a different applications such as ultraviolet (UV) light-emitting devices (G. Deng et al., 2020), photocatalytic degradation, chemical and bio sensing (Aad et al., 2013). Further, to control the uniformity and density of NWs, high temperature vacuum-chamber deposition techniques have been traditionally used. However, these methods face significant limitations: (i) they require expensive and complex equipment, increasing the cost and complexity of the final device, and (ii) they are incompatible with flexible substrates due to the high temperatures involved. To meet the growing demand for flexible electronics, researchers are turning to aqueous synthesis routes that utilize low-temperature chemical reactions to grow ZnO NWs. One promising approach is the CBD technique.

CBD has attracted interest as a low-temperature method for precisely altering the structural morphology of ZnO nanostructures, particularly NWs, on flexible substrates through selective area growth. In the process, the morphology of ZnO nanostructures can be adjusted by varying key growth parameters such as precursor concentration, growth time, and temperature.

However, the Zn-salt based seed layer necessary for ZnO crystal nucleation typically requires high-temperature sintering (~ 400 °C). However, with the advancement of flexible electronics, substrates with different properties cannot support high-temperature seed sintering, altering the effects of growth parameters on NWs. Previously published literatures predominantly focuses on conventional substrates, leaving a substantial gap in understanding how flexible substrates (critical for wearable sensing applications), affect the growth process of NWs (Huang et al., 2020). As a result, metal-assisted synthesis of NWs, which does not require high-temperature seed sintering, has received an increasing attention. Therefore, a deeper understanding of the growth mechanisms is essential and could significantly aid in the metal seeded growth of NWs. Further, the use of parametric analysis, along with methods such as analysis of variance (ANOVA) and ML, is important for optimizing the growth process. ML allows researchers to explore datasets, enabling the classification of observations, identification of key performance-influencing features, and prediction of outcomes in novel experiments. In less data-intensive fields, ML assists in optimizing experiment design for improved performance. In nanotechnology, ML methods are expected to set new standards, transforming data collection, analysis, and interpretation. Simultaneously, nanotechnology holds potential for advancing ML through the development of electronic devices that execute algorithms more efficiently than traditional computing architectures (Brown et al., 2020). Previously, researchers used statistical and modelling techniques to optimize and predict the characteristics using response surface methodology (RSM) (Neumann et al., 2010) and artificial neural network (ANN) (Esmailzadeh-Gharedaghi et al., 2012). Researchers can use ANOVA to systematically investigate the simultaneous effects of multiple growth factors on predictability and repeatability of the synthesis process by studying the variations in diameter and length of NWs. In addition, ANN offer effective instruments for analyzing large datasets and extracting intricate patterns from experimental data. Researchers can train ML models on large datasets containing a wide range of growth parameters and corresponding NWs characteristics to develop predictive models that capture the complex relationships between different variables. The use of ML with parametric analysis not only broadens the understanding of ZnO NWs growth, but also opens up possibilities for optimizing and automating the synthesis process.

In this study, we present a comprehensive and systematic investigation of the direct growth of ZnO NWs on flexible PET substrates using Ag-seeded growth, without the need for high-temperature seed sintering. Utilizing statistical and machine learning models as predictive tools, we develop a detailed growth diagram that examines the variations in diameter and length of ZnO NWs with respect to fundamental growth parameters. This approach reveals the high potential of Ag-seeded ZnO NWs for both applied research and industrial applications.

2.1.2 Experimental Section

(a) Synthesis of ZnO NWs

A standardized cleaning protocol was used to prepare the polyethylene terephthalate (PET) substrate prior to metal seed deposition. The substrate undergoes a sequential cleaning process in isopropyl alcohol (IPA) and deionized water (DI) water under sonication for 15 min to eliminate any contaminants and dust. Following the cleaning step, a 25 nm layer of Silver (Ag) was deposited onto the PET substrate using a thermal evaporation system (ME300 evaporator from PLASSYS, France). The Ag seeded PET was then subjected to a 5 min treatment involving UV- ozone exposure (Jolight Company Inc, USA) to oxidize the Ag layer. In addition, a precursor solution is prepared by combining zinc acetate (ZnAc; Molecular weight: 219.51g/mol) and hexamethylenetetramine (HMTA; Molecular weight: 140.186 g/mol) in a 1:1 ratio, with concentrations ranging from 15 mM to 35 mM. The solution was then transferred to a 3-neck flask as a reaction vessels connected with a thermocouple, stirrer, and a Teflon sample holder as shown in Figure 2.1. The Ag seeded PET was then carefully immersed in the precursor solution. For the growth phase, the temperature was controlled using a PID controlled heating mantle (fisher scientific; UK), maintained between 75–95°C for a varying duration of 30–60 mins. After the

growth process was completed, the samples were cooled, washed twice with DI water, and dried using an air gun. The growth parameters were selected based on a comprehensive review of the literature, which indicates that precursor concentration, growth time, and temperature are the most critical factors for the growth of ZnO NWs (Azmi et al., 2022; Hou et al., 2014). These parameters have a direct and substantial impact on the nucleation process, growth kinetics, morphology, and overall quality of the nanowires. By optimizing these parameters, researchers can achieve the desired structural and functional properties in ZnO NWs, making these factors crucial for understanding growth mechanisms and tailoring the nanowires for specific applications, such as gas sensing.

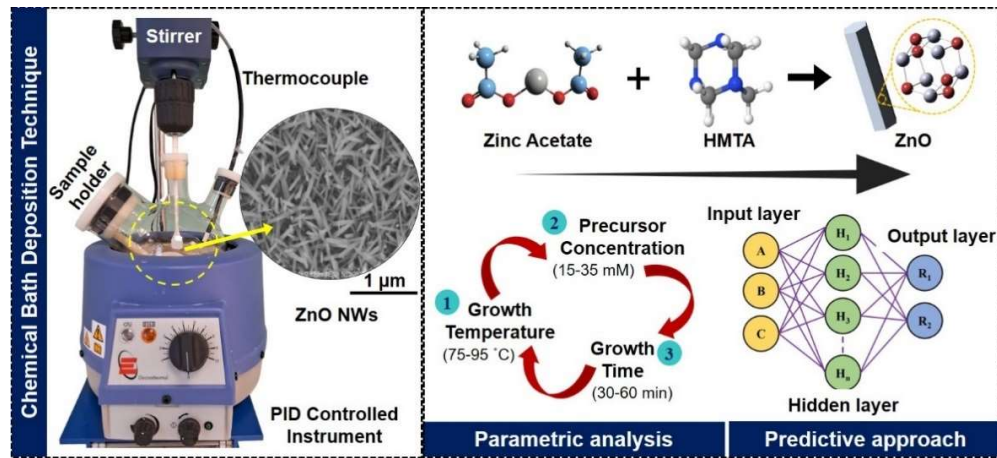


Figure 2.1: Schematic representation of CBD technique

(b) Machine Learning and ANOVA

Response Surface Methodology (RSM)

The RSM is a technique commonly used in experimental designing to optimize various processes statistically. This process includes performing experiments, building models, evaluating the influence of different parameters, and ultimately identifying the operating conditions that require the fewest number of experiments. In this study, the central composite design (CCD) was utilized to determine the best conditions for NWs growth and predict the diameter and length of NWs. Here, the diagonal of the hexagonal NWs is considered as the diameter of the NWs. The approach took into account three key factors: (A) precursor concentration, (B) growth time, and (C) growth temperature. To achieve statistical analysis, Design-Expert software was used. This enabled researchers to execute techniques such as ANOVA, generate 3D surface plots, and calculate fit statistics. The CCD design involved three levels for each parameter, ensuring a defined range of experimentally independent parameters listed in Table 2.1 below. The key aim of the polynomial regression equation was to establish and illustrate the relationship between the variables and the corresponding responses. This equation serves as a mathematical model that enables exploration of how the independent variables influence the dependent responses in the investigation. The experimental data presented in Table 2.2 was analyzed using a regression (response surface) approach to address a second-order polynomial problem (see Eq. 2.1):

$$R_m = C_0 + \sum_{m=1}^k C_m F_m + \sum_{m=1}^k C_{mm} F_m^2 + \sum_{m=1}^{k-1} \sum_{n=m+1}^k C_{mn} F_m F_n \quad (2.1)$$

where, R_m represents the response (in this study diameter and length of NWs). C_0 , C_m , and C_{mn} are coefficients of the model, while F_m and F_n denote the independent process variables.

Table 2.1: Three operating parameters used in CCD modelling

Factors (F)	Operating Parameters	Units	Range
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			-1	0	+1
F1:A	Precursor concentration	mM	15	25	35
F2:B	Growth time	mins	30	45	60
F3:C	Growth temperature	°C	75	85	95

Artificial Neural Network (ANN)

A standard ANN is made up of three interconnected layers: an initial layer that contains the distinct factors acting independently, a final layer that depicts the corresponding responses, and an intermediate hidden layer that contains a specific number of nodes that establish connections between the initial and final layers. The model was trained using MATLAB R2023b, which included the neural network fitting tool as well as the Levenberg-Marquardt backpropagation algorithm. The model was built with a two-layer feed-forward neural network, with hidden neurons using sigmoid activation and linear output activation. A total of 80% of the dataset was designated for training, while 10% was used for validation and another 10% for testing. The model was trained through multiple iterations until the optimal number of neurons for the hidden layer was determined to be 8. The coefficient of determination (R^2) and the mean square error (MSE) were computed using specific equations to assess the efficiency of the ANN (see equation 2.2). The training process concluded automatically if the MSE of the validation set started to increase.

$$MSE(\%) = (\sum_{m=1}^N (O_E - O_P)^2 / N) \quad (2.2)$$

Table 2.2: Designed matrix with actual and predicted results obtained using RSM and ANN models for determining the diameter and length of NWs

Run	Factors			Diameter (nm)			Length (nm)		
	A	B	C	Actual	Predicted		Actual	Predicted	
					RSM	ANN		RSM	ANN
1	25	60	75	175.71	158.91	171.31	653.78	547.32	587.12
2	35	30	75	103.27	93.08	101.71	298.67	349.03	279.86
3	15	60	75	41.98	45.72	35.88	573.65	687.52	560.31
4	25	45	85	173.67	167.83	171.04	980.43	1161.50	1024.75
5	15	60	85	99.27	92.36	98.02	1532.46	1496.79	1505.94
6	35	45	85	191.62	211.60	187.34	1204.89	1237.80	1297.16
7	15	30	95	37.51	38.87	54.96	843.65	841.32	658.35
8	25	30	95	79.18	70.06	75.87	685.57	749.29	812.16
9	25	30	85	169.47	190.41	162.28	802.7	858.01	747.27
10	35	60	75	208.07	243.67	200.21	588.07	599.54	511.99
11	35	30	85	179.88	183.70	155.28	1168.6	1012.75	1126.53
12	35	60	85	362.57	309.25	218.41	1347.78	1300.13	1419.86
13	25	60	85	195.49	215.02	204.68	1256.5	1302.25	1289.27
14	25	45	75	102.09	99.20	103.27	575.79	425.00	357.54
15	15	45	85	93.84	95.64	90.07	1353.49	1277.62	1235.57
16	25	45	95	58.94	34.96	59.99	1178.49	1071.21	1200.65
17	25	60	95	51.45	69.61	40.01	1211.7	1230.39	1364.82
18	35	30	95	79.64	72.82	81.68	860.88	849.67	1019.3

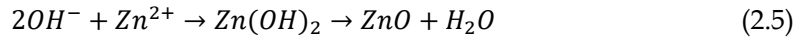
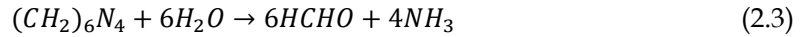
19	35	45	95	67.79	88.18	71.83	1054.76	1093.17	1260.95
20	35	45	75	142.96	133.50	140.36	474.09	555.65	407.81

Factors: A (Precursor concentrations; mM), B (Growth time; min), and C (Growth temperature; °C)

2.1.3 Results and Discussions

(a) Growth Mechanisms of ZnO NWs

The Ag-assisted growth mechanism of ZnO NWs results from the interaction between the oxidized Ag surface and ZnO precursors. The Ag₂O layer offers a surprisingly well-matched lattice structure with ZnO. The ionized Ag surface attracts negatively charged Zn ion complexes via Coulombic forces, promoting ZnO nucleation on the Ag₂O substrate (Kim and Kwon, 2014). Additionally, CBD growth method involves three stages: (i) generation of atomic, molecular, or ionic species, (ii) diffusion of these species through a medium, and (iii) condensation of the species. The synthesis of ZnO NWs from precursors: ZnAc and HMTA is driven by the following reactions (Xu et al., 2009).



Moreover, the role of HMTA is important as it is a non-cyclic tertiary amine which has a high strain energy molecular structure, it can be understood to lighten the role of a bidentate Lewis base to coordinate and bridge two Zn²⁺ ions (Chen and Li, 2022), which assist in controlling the amount of Zn²⁺ free ions in the solution and thus stabilizing it (Ashfold et al., 2007). As shown in equations (2.3 to 2.5), HMTA has a lot of molecular rigidity and so it readily hydrolyses in water to slowly release formaldehyde HCHO and ammonia NH₃. The slow release of NH₃ has three important roles to play in the synthesis. The slow release of NH₃ assists slow release of OH⁻ thus enabling the minimization of bulk nucleation of Zn²⁺ in the solution (McPeak et al., 2011); secondly the basic environment formed through the formation of OH⁻ is necessary for the formation of Zn(OH)₂ which eventually dehydrates to form ZnO under heated conditions (Liang et al., 2014) and thirdly it coordinates with the Zn²⁺ ions present in the solution causing them to stabilize in solution thus making them available for heterogeneous precipitation at the substrate surface. The final possible hypothesis of the role of HMTA is derived from the fact that it attaches to the non-polar faces of the wurtzite crystal geometry, thus accelerating and accentuating the growth along the polar (0001) face (Xu and Wang, 2011). Furthermore, metal oxides tend to hydrolyse when exposed to water, resulting in the formation of a hydroxide layer. Through surface amphoteric reactions, this layer can acquire a charge by interacting with H⁺ or OH⁻ ions (Degen and Kosec, 2000). As a result, Ag⁺ ions on the Ag₂O surface have the potential to form Ag-OH bonds. Intriguingly, both Ag⁺ and Zn²⁺ ions are classified as B-type metal cations with low electronegativities (Stumm et al., 1992), i.e., in the case of Ag-OH, the bond length of Ag-O is shorter than that of O-H because Ag is less electronegative than H. In water, OH⁻ can convert Ag-OH into Ag-O⁻ and H₂O. Simultaneously, Zn²⁺ ions with low electronegativity have a tendency to bond readily, resulting in the formation of Ag-O-Zn⁺ interactions. When Zn⁺ ions are chemisorbed onto the Ag₂O surface, they form bonds with oxygen ions, resulting in ZnO. As a result, ZnO clusters can completely cover the Ag₂O surface on the substrate, allowing for the controlled growth of ZnO NWs.

(a) Design of Experiments for Controlled Growth of ZnO NWs

Regression Model

A total of 20 experiments were performed in a random order by varying the operating parameters (see Table 2.2). The result obtained from the experiment is categorised in two outputs such as R₁: Diameter and R₂: Length of NWs in the ranges from ~37 to ~363 nm and ~299 to ~1532 nm, respectively. The Design Expert software offers the quadratic regression model with the following equations 2.6 and 2.7, which were obtained for the diameter and length of NWs, respectively, and validated by ANOVA with variables having a p-value <0.05.

$$\text{Diameter } (R_1) = +167.56 + 57.88 \times A + 12.46 \times B - 32.43 \times C + 50.69 \times AB + 9.76 \times AC - 11.98 \times BC - 13.63 \times A^2 + 34.77 \times B^2 - 100.81 \times C^2 \quad (2.6)$$

$$\text{Length } (R_2) = +1161.50 - 19.91 \times A + 222.12 \times B + 323.10 \times C - 78.43 \times AB - 54.34 \times AC + 18.44 \times BC + 96.21 \times A^2 - 81.37 \times B^2 - 413.39 \times C^2 \quad (2.7)$$

where A, B, and C represent the precursor concentration, growth time and growth temperature, respectively. Positive model values signifies the positive effect of variables on the responses R₁ and R₂, whereas a negative model represents the negative effects of the variables on R₁ and R₂ responses.

ANOVA for Quadratic Model

Both RSM and CCD based models for the ANOVA showed statistically significant outcomes. The corresponding results are displayed in Tables 2.3 and 2.4, for diameter and length of ZnO NWs, respectively. The Fisher variance ratios (F-ratios) for nanowire's diameter and length are 16.67 and 15.99, respectively, indicating that there is only a 0.01% chance of noise signals resulting in an F-value in the model, proving that the model is significant and acceptable. The ANOVA analysis verified the predicted model's accuracy for nanowire's diameter. With a 95% confidence level, a p-value of 0.0001 (<0.05) indicated the significance of model components, with terms A, C, AB, B², and C² having significant effects on nanowire's diameter. In addition to the p-value, other statistical metrics such as adequate precision (Ad. Pr.), standard deviation (Std. Dev.), and correlation coefficient (R²) were used to evaluate the effectiveness of the model. Adequate precision (Ad. Pr.) is a factor used in the model to compute the signal-to-noise ratio (preferred to be >4). The Ad. Pr., Std. Dev., and R², values are 14.39, 27.06, and 0.94, respectively, indicating that the regression models are significant. Figure 2.2 depicts the 2D and 3D response plots for the diameter of NWs obtained at different growth temperatures.

Table 2.3: CCD design results using ANOVA technique for diameter of NWs

Source	Sum of Squares	Df*	Mean Square	F-value	p-value	
Model	1.098E+05	9	12200.97	16.67	< 0.0001	significant
A-Precursors Concentration	28069.08	1	28069.08	38.35	0.0001	
B-Growth Time	1051.04	1	1051.04	1.44	0.2584	
C-Growth Temperature	6183.75	1	6183.75	8.45	0.0157	
AB	7640.89	1	7640.89	10.44	0.0090	
AC	243.43	1	243.43	0.3326	0.5769	
BC	530.54	1	530.54	0.7248	0.4145	
A ²	748.56	1	748.56	1.02	0.3357	
B ²	4281.30	1	4281.30	5.85	0.0362	
C ²	41276.89	1	41276.89	56.39	< 0.0001	
Residual	7319.95	10	731.99			
Cor Total	1.171E+05	19				
Standard Deviation = 27.06, R ² = 0.94, Adjusted R ² = 0.88, Adequate Precision = 14.39						

*Df= degree of freedom

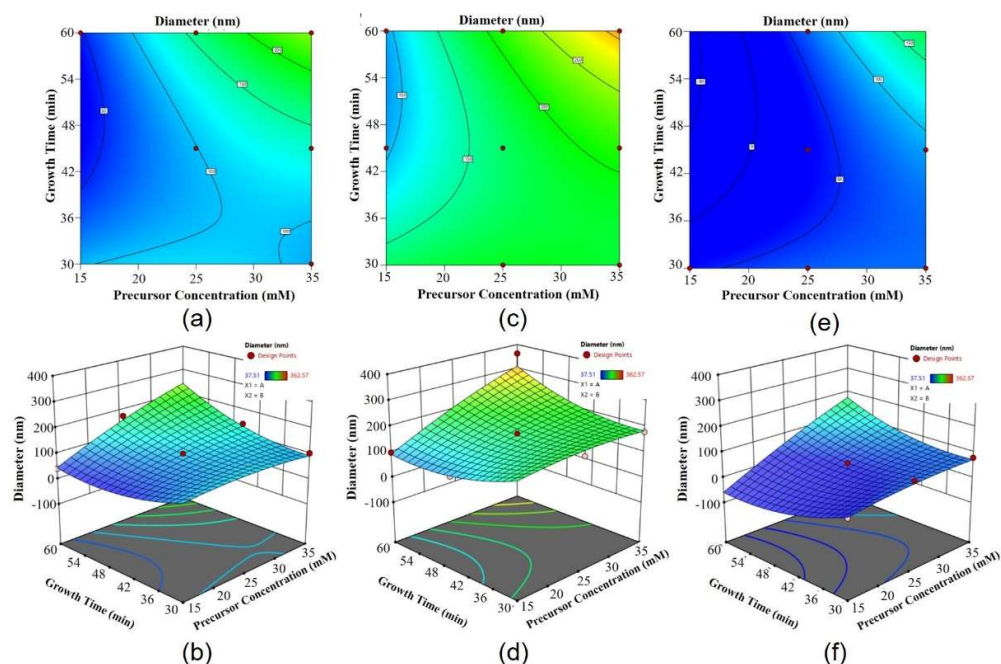


Figure 2.2: 2D and 3D response plots illustrating the impact of precursor concentration and growth time on the diameter of NWs at varying growth temperatures: (A,B) 75°C, (C,D) 85°C, and (E,F) 95°C

Table 2.4: CCD design results using ANOVA technique for length of NWs

Source	Sum of Squares	Df*	Mean Square	F-value	p-value	
Model	2.109E+06	9	2.343E+05	15.99	< 0.0001	significant
A-Precursors Concentration	3319.73	1	3319.73	0.2266	0.6443	
B-Growth Time	3.341E+05	1	3.341E+05	22.81	0.0008	
C-Growth Temperature	6.137E+05	1	6.137E+05	41.89	< 0.0001	
AB	18292.55	1	18292.55	1.25	0.2899	
AC	7554.45	1	7554.45	0.5157	0.4891	
BC	1255.63	1	1255.63	0.0857	0.7757	
A ²	37325.67	1	37325.67	2.55	0.1415	
B ²	23451.31	1	23451.31	1.60	0.2345	
C ²	6.941E+05	1	6.941E+05	47.38	< 0.0001	
Residual	1.465E+05	10	14649.40			
Cor Total	2.255E+06	19				

Standard Deviation = 121.03 , R² = 0.94 , Adjusted R² = 0.88 , Adequate Precision = 13.41

*Df= degree of freedom

In the case of the length of the NWs length, the models' p-value is 0.0001, indicating that the model components with terms B, C, and C² have significant effects on NW's length. The Ad. Pr., Std. Dev., and R² values are 13.41, 121.03, and 0.94, respectively, indicating that the regression models are significant. Figure 2.3 depicts the 2D and 3D response plots for the length of NWs at different growth temperatures.

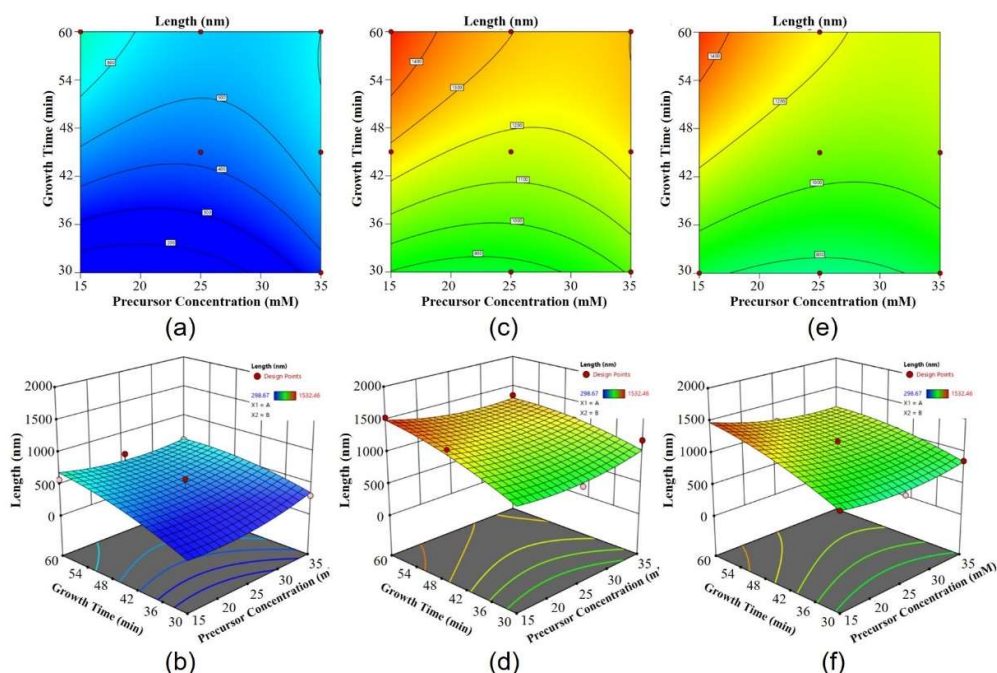


Figure 2.3: 2D and 3D response plots showing the correlation between precursor concentration and growth time on the length of NWs at varying growth temperatures: (A,B) 75°C, (C,D) 85°C, and (E,F) 95°C

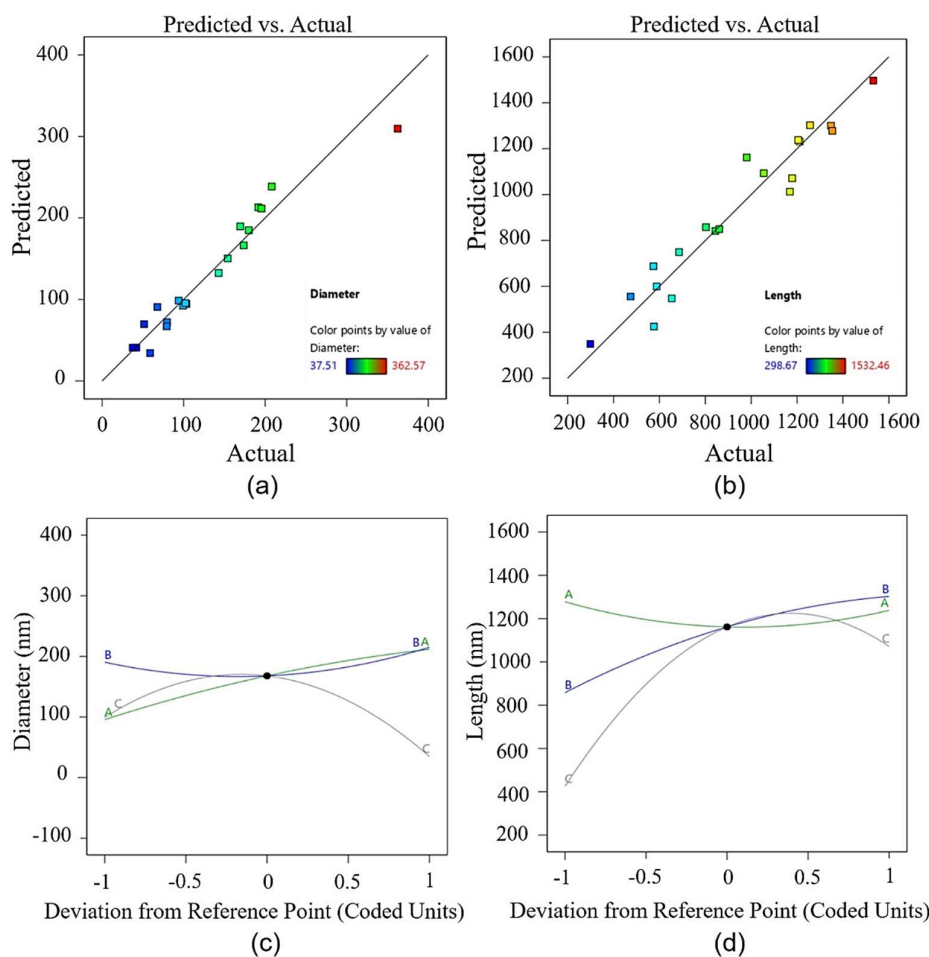


Figure 2.4: Graphical relationship between experimental vs. predicted results for (a) diameter, and (b) length of NWs obtained by using design expert software, and (c, d) perturbation plots

(b) Parity and Perturbation Plot

The effectiveness of selecting different operating variables and accuracy of the RSM model can be determined using a parity plot which is used to represent a correlation between actual and predicted values of the experiment. Figure 2.4 (a-b) shows the relationship between the predicted and actual experimental responses obtained for both outputs (diameter and length of NWs). The predicted values of the model were found to match the actual values as the majority of values are along the diagonal line, demonstrating the model's efficiency in removing ambiguous and inaccurate outcomes. Further, the perturbation plot is a useful tool for evaluating the impact of different factors within a given design space (see Figure 2.4 (c-d)). Stat-Ease sets the reference point to the centre (coded 0) of all the factors by default. When dealing with multiple factors, the perturbation plot is especially useful for identifying the factors that have the greatest influence on the response. A steep curve in relation to a particular factor indicates that the response is highly sensitive to changes in that factor, whereas a relatively flat line indicates that changes in that factor have little or no effect on the response. Figure 2.4 (c, d) clearly shows that Factor C and Factor B, corresponding to the growth temperature and growth time, are the primary factor influencing the diameter and length of NWs, respectively.

(c) Effects of Various Growth Conditions

IMAGE J software was utilized to measure the average diameter and length of the NWs. The diameters are measured directly from the top-view FESEM images, while the length was measured by scratching the sample with a tweezer to remove the NWs from the sample, followed by measurement of the distorted NWs. Moreover, the impact of these growth conditions is discussed in the following subsection.

Influence of Growth Temperature

The length and diameter can be affected by the temperature of the growth solution. The results depicted in the figure 2.5 illustrates the CBD growth of ZnO NWs at different temperatures (75-95°C), while maintaining a fixed growth time of 30 min and a precursor concentration of 15 mM. The results show that with the increase in growth temperature from 75°C to 95°C, the diameter of ZnO NWs decreases while the length tends to increase. Previous articles have reported that at lower temperatures between 60-70°C, ZnO nanostructures exhibit incomplete development and begin transitioning towards 1D structures as the temperature increases to 75°C which can be seen in Figure 2.5 (a, d). Optimal conditions are observed at 85°C in our experimental setup, where high-density uniform ZnO NWs structure are grown, having a diameter of ~43 nm. Figure 2.5 (b, e) reveals the hexagonal cross-section indicative of wurtzite ZnO crystal growth as evident from the XRD plot. As the growth temperature further increases, the overall morphology of ZnO NWs tends to show a reduction in the diameter to ~38 nm and a lower density. The relationship between the diameter, length and density of ZnO NWs with the growth temperature is depicted in Figure 2.6. The density of NWs is calculated by measuring the number of NWs present per microns. The length of the NWs increases steadily as the temperature rises from 85°C to 95°C, while their diameter remains nearly constant. This indicates that higher temperatures increase the reaction kinetics, leading to a rapid precipitation of ZnO, thus obtaining longer, and higher aspect ratio NWs. It is also observed that lower temperatures results in non-NWs structures such as nanoplates and nanoflowers, while excessively high temperatures lead to higher diameter ZnO NWs with decreased density (Abeykoon et al., 2023). Furthermore, we observed that the density of ZnO NWs is highest at 85°C but decreases again at a growth temperature of 95°C. This observation is consistent with the findings of Xu et al., who reported that the NW density decreases at both lower (60°C) and higher (95°C) temperatures compared to moderate temperatures (Xu et al., 2008). This phenomenon can be attributed to several factors: Firstly, as the temperature increases, the growth rate of individual nanowires may accelerate, leading to the consumption of available precursor material. At 95°C, the faster growth rate could reduce the availability of material for new nucleation, thus decreasing the NW density. Secondly, at higher temperatures, a process known as Ostwald ripening may occur, where smaller NWs

dissolve and larger NWs continue to grow until equilibrium is reached. This process reduces the overall density of nanowires (Alshehri et al., 2018). Additionally, at higher temperatures, Zn atoms adhering to the surface exhibit higher mobility, which can result in the coalescence of nanowires. This coalescence reduces the number of distinct nanowires as they merge into fewer, larger structures (ElZein et al., 2023). Hence, we have selected 85°C as the standard growth temperature in our experimental setup, as it yields high-density arrays of ZnO NWs compared to other temperature conditions. Table 2.5 presents the summary of diameter, length and aspect ratio of NWs obtained at different growth temperature but at fixed 15 mM precursor concentration and at a growth time of 30 mins.

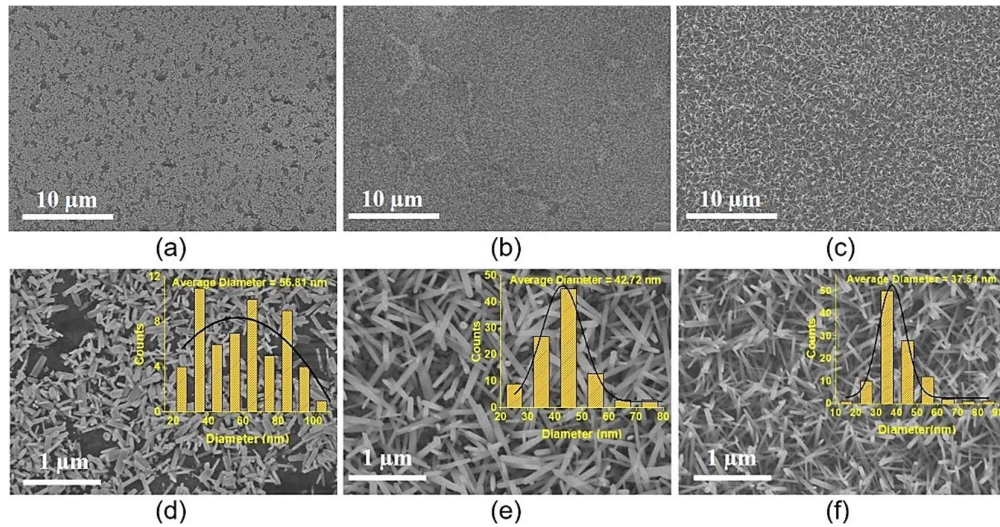


Figure 2.5: FESEM images of ZnO NWs growth on oxidised Ag/PET substrate with precursor concentration maintained at 15 mM for 30 mins and at varying temperatures (a, d) 75°C, (b, e) 85 °C and (c, f) 95 °C, with inset images representing the histogram of average diameter calculated after at least 80 counts of nanowires

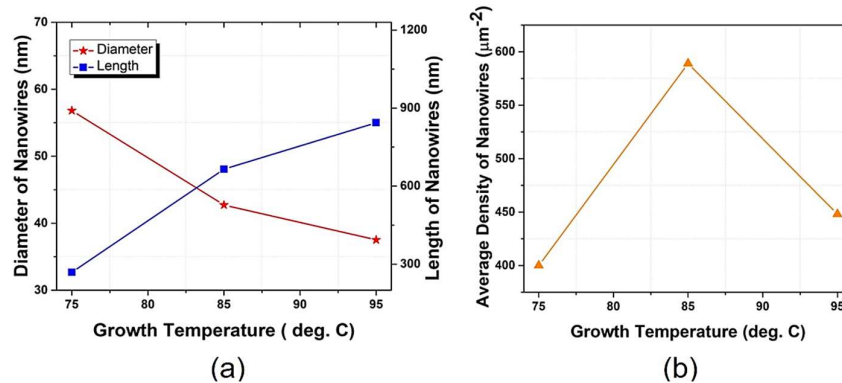


Figure 2.6: Plot showing (a) diameter of NWs and (b) density of NWs at different growth temperatures

Table 2.5: Summary of ZnO NWs growth conditions for diameter, length, and aspect ratio at three different growth temperatures with a 15 mM precursor concentration and at 30 mins growth period

Growth Temperature	Growth Time	Precursors concentration	Diameter (nm)	Length (nm)	Aspect ratio
75°C	30 mins	15 mM	56.81	268.56	4.73
85°C			42.72	665.13	15.57
95°C			37.51	843.63	22.49

Influence of precursor Concentration

It is interesting to know how an increasing or decreasing precursor concentration will eventually influence the resultant products. Previously, researchers obtained ZnO microrods at higher precursor concentrations, whereas a relatively lower precursor concentration tends to deliver ZnO NWs. This suggests that precise control of the initial precursor concentration can be leveraged to directly influence the dimensions of the resulting ZnO NWs. Figure 2.7 depicts the FESEM images of ZnO NWs grown at varying precursor concentrations (15-35 mM), while maintaining a fixed growth temperature of 85°C and a growth time of 30 min. It is observed that at low concentration (15 mM) the ZnO NWs which are closely packed have a smaller diameter of ~43 nm. As the precursor concentration increases to 25 mM and 35 mM, the diameter of NWs increases to ~169 nm and ~180 nm, respectively. The relationship between the diameter, length and density of ZnO NWs with the precursor concentration is depicted in Figure 2.8.

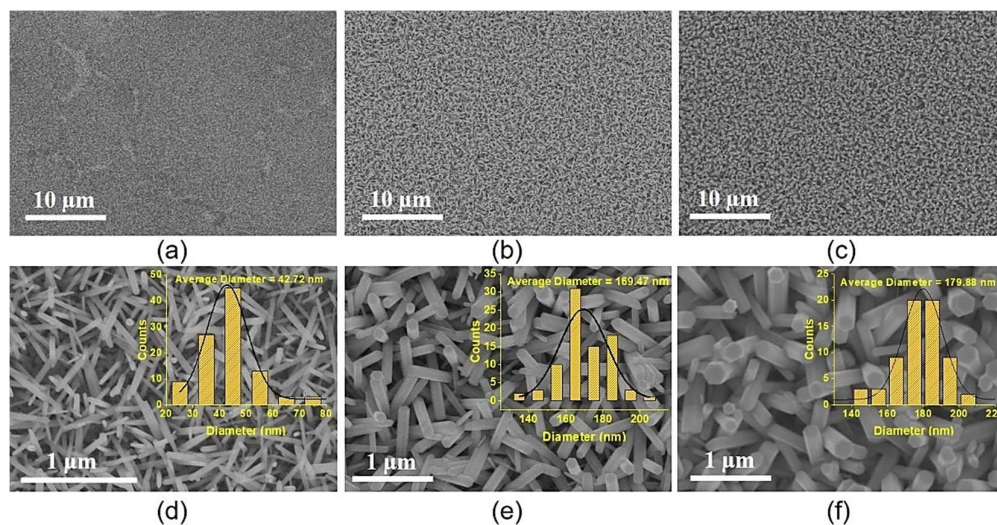


Figure 2.7: FESEM images of ZnO NWs growth on oxidised Ag/PET substrate at a fixed 85°C for 30 min and at three precursor concentrations, namely, (a, d) 15 mM, (b, e) 25 mM and (c, f) 35 mM, respectively, with inset images representing the histogram of average diameter calculated after at least 80 counts of nanowires

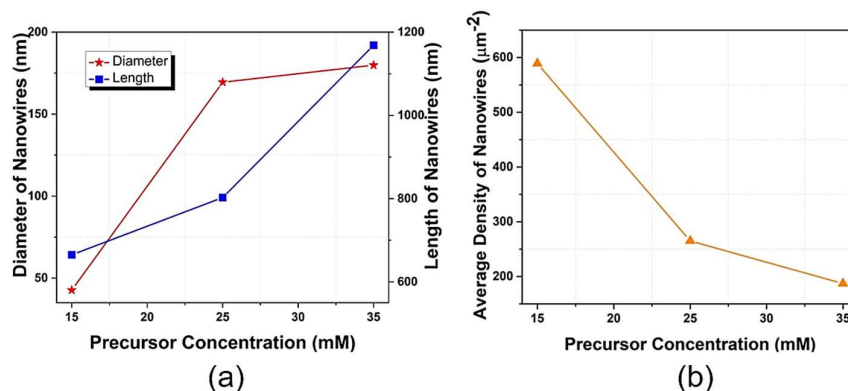


Figure 2.8: Plots showing (a) diameter of NWs and (b) density of NWs at different precursor concentrations

The length of the NWs nearly doubled as the precursor concentration increases from 15 mM to 35 mM, while the density of ZnO NWs significantly decrease from 589 to 187 μm⁻² as the diameter increases from ~43 to ~180 nm. It was also observed that the ZnO NWs having different diameters can be obtained when the precursor concentration is varied, even though the operating conditions are maintained the same. The phenomenon can be elucidated through the lattice orientation effect (Devaraj et al., 2016). According to this effect, as ZnO NWs grow, nucleus formation typically aligns along the c-axis at nucleation sites. If secondary nucleation occurs, the lattice plane of the developing NWs starts to align parallel to that of neighboring NWs.

Consequently, particles at the interface merge in the direction of growth, promoting lateral growth. This alignment effect fosters the coalescence of adjacent NWs, ultimately yielding ZnO NWs with increased diameters. Furthermore, NWs synthesized at 35 mM had a lower aspect ratio compared to those at 15 mM, which can be attributed to non-polar face growth being less inhibited at high precursor ions concentration, leading to faster ZnO NWs diameter growth than at lower concentrations. Table 2.6 summarizes the results of ZnO NWs obtained at different precursor concentrations after 30 min of growth at 85°C.

Table 2.6: Summary of ZnO NWs growth conditions for diameter, length, and aspect ratio at three different precursor concentration with a fixed growth temperature of 85°C for a 30 mins growth period

Precursor concentration	Growth Time	Growth Temperature	Diameter (nm)	Length (nm)	Aspect ratio
15 mM	30 mins	85°C	42.72	665.13	15.57
25 mM			169.47	802.70	4.73
35 mM			179.88	1168.60	6.50

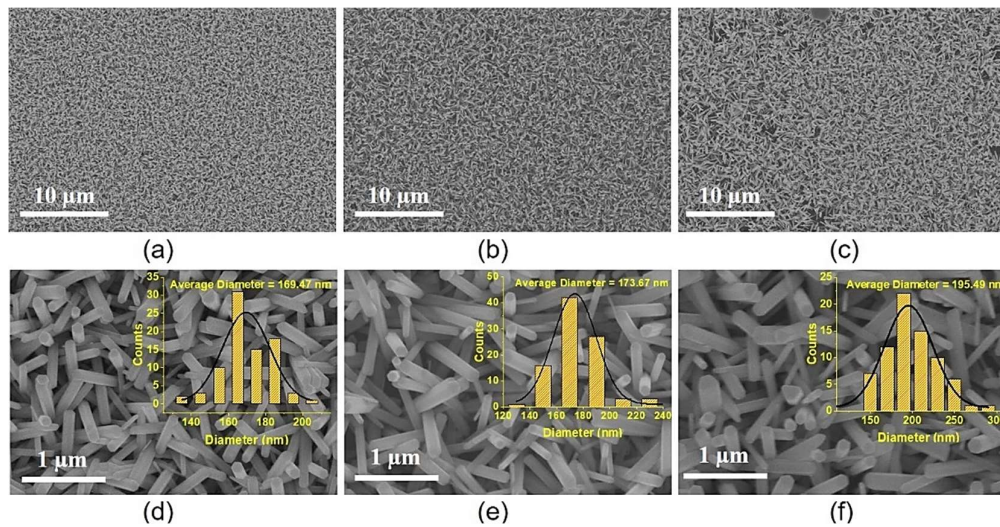


Figure 2.9: FESEM images of ZnO NWs grown on oxidised Ag/PET substrate at a fixed 85°C in 25 mM precursor concentration, and at varying growth time (a, d) 30 mins, (b, e) 45 mins, and (c, f) 60 mins, with inset images representing the histogram of average diameter calculated after at least 80 counts of nanowires

Influence of Growth Time

Figure 2.9 depicts the FESEM images of NWs grown via CBD at varying growth times (30-60 mins), while maintaining a fixed growth temperature of 85°C and a precursor concentration of 35 mM. Previous research shows that the length of NWs is influenced by the growth time. Figure 2.9 (a, d) shows FESEM image of NWs grown for 30 mins, with average diameters and lengths of ~169 and ~803 nm, respectively, indicating the emergence of wires at nucleation sites. These initial NWs continue to grow with increase in growth duration. After 45 mins, there is minimal change in diameter, but the length increases to ~980 nm (Figure 2.9 (b, e)). Extending the growth time to 60 mins results in further lengthening of NWs to ~1.25 μm, accompanied by a slight increase in diameter (Figure 2.9 (c, f)). Previous studies have shown a similar trend of axial growth as compared to lateral growth with an increase in the growth time (Pei et al., 2010). This long growth time have resulted in the ZnO NWs growth along c-axis of the polar direction (001) (Mosalagae et al., 2020). The relationship between the diameter, length and density of NWs with the precursor concentration is depicted in Figure 2.10. The length of the NWs changed from ~803 to ~1257 nm as the growth time increased from 30 mins to 60 mins, while the density of ZnO NWs slightly decreased from 233 to 159 μm⁻² with a small increase in diameter from ~169 to ~195 nm. Table 2.7 summarizes the results of NWs obtained at different growth time.

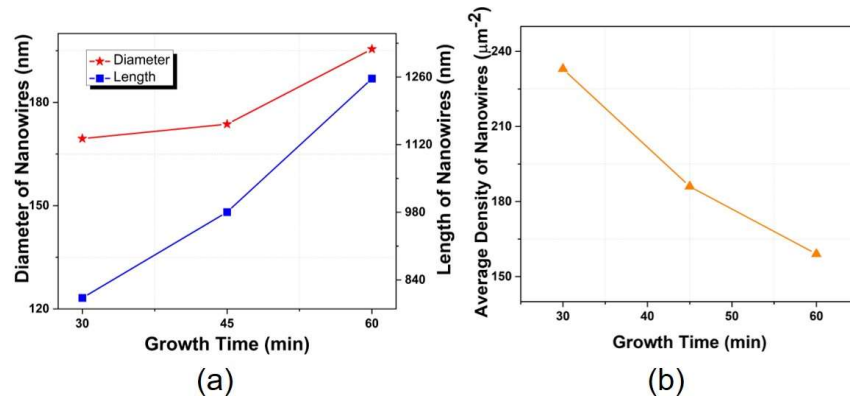


Figure 2.10: Plot showing (a) diameter of NWs and (b) density of NWs at varying growth periods

Table 2.7: Summary of ZnO NWs at three different growth time for diameter, length, and aspect ratio with a fixed precursor concentration and growth temperature of 25 mM and 85°C, respectively

Growth Time	Growth Temperature	Precursors concentration	Diameter (nm)	Length (nm)	Aspect ratio
30 min	85°C	25 mM	169.47	802.70	4.73
45 min			173.67	980.43	5.64
60 min			195.49	1256.65	6.43

Figure 2.11 shows the X-ray diffraction (XRD) patterns of NWs grown on a flexible substrate, which were recorded at room temperature, covering a 2θ range from 20° to 80° using Cu K1 α radiation with a wavelength of 1.54059 Å. The dominant peak corresponding to the PET substrate emerged at $2\theta = 26^\circ$, exhibiting notably higher intensity compared to other PET related peaks (Faraj and Ibrahim, 2011). Additionally, the XRD analysis successfully identified characteristic peaks attributed to Ag₂O at $2\theta = 37.4^\circ$, 43.12° , and 55.86° , as similarly reported by Yong et al (Ng et al., 2016). Prominent ZnO peaks were identified, including the (100) plane at $2\theta = 31.86^\circ$, the (002) plane at $2\theta = 34.44^\circ$, and the (101) plane at $2\theta = 36.26^\circ$. The collective patterns strongly indicate the presence of a hexagonal wurtzite crystalline structure. Similar peaks were noted in prior studies, highlighting their alignment with the standard JCPDS 01-089-0510 data file (Jabeen et al., 2014).

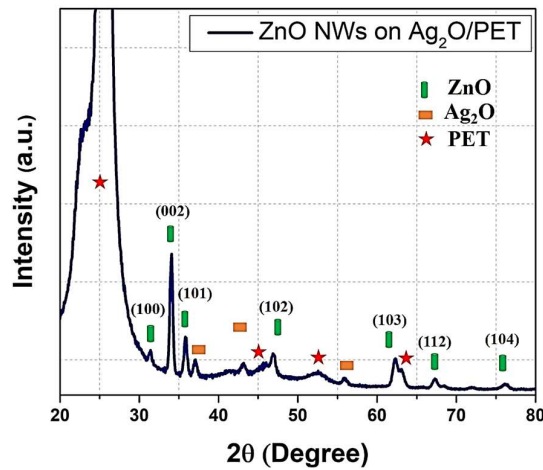


Figure 2.11: XRD spectra of ZnO NWs grown on flexible substrate

(d) ANN Modeling

The ANN architecture composes of three neurons (i) input layer representing precursor concentration, growth time, and growth temperature, (ii) hidden layer and, (iii) an output layer

with two neurons corresponding to the diameter and length of the ZnO NWs. The ANN model utilized the given experimental data points, out of which, 80% of the dataset was designated for training, while 10% was used for validation and another 10% for testing. Following several iterations, the model was trained to optimize the number of neurons in the hidden layer, eventually settling on 8 neurons. Notably, mean squared error (MSE) values for diameter and length were calculated. MSE values of 20.51 and 1054.3 were obtained for the diameter during training and validation, respectively. In contrast, the corresponding MSE values NW's length were 1303.2 (training) and 1421.9 (validation). The validation results confirm the model's reliability, indicating its potential as a predictive tool for both the diameter and length of NWs. Figure 2.12 depicts relationship between predicted and actual experimental results. Overall correlation coefficients (R^2 values) for diameter and length are 0.925 and 0.961, respectively.

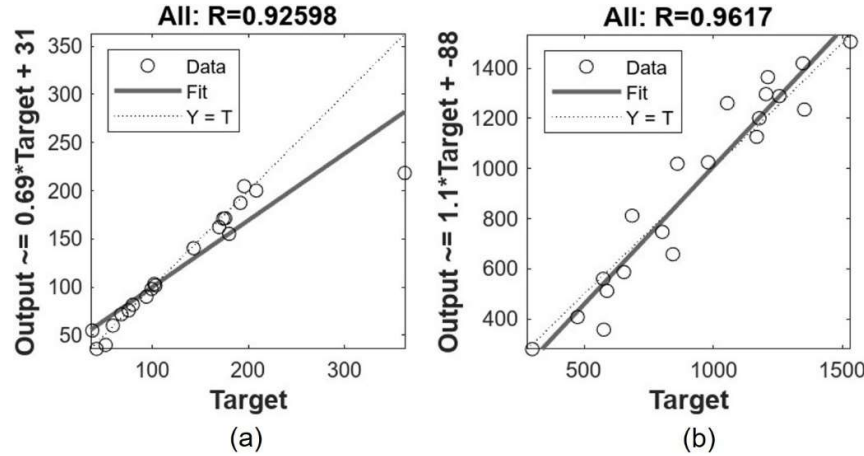


Figure 2.12: Graphical relationship between experimental vs. predicted results for (a) diameter, and (b) length of NWs

To validate the model, three values were chosen within the designated range of operational parameters. Amongst these, an experimental trial was conducted under optimized operating conditions: precursor concentration of 15 mM, growth time of 30 min, and growth temperature of 75°C. The experimental result depicts that an actual nanowire's diameter is $\sim 57 \pm 2$ nm and the length is $\sim 269 \pm 12$ nm. In comparison, RSM predicted values were ~ 108.56 nm for diameter and ~ 129.96 nm for length. Whereas ANN prediction yielded diameter and length values of ~ 70.32 nm and ~ 185.29 nm, respectively. These predictions were subsequently validated against the experimentally obtained data.

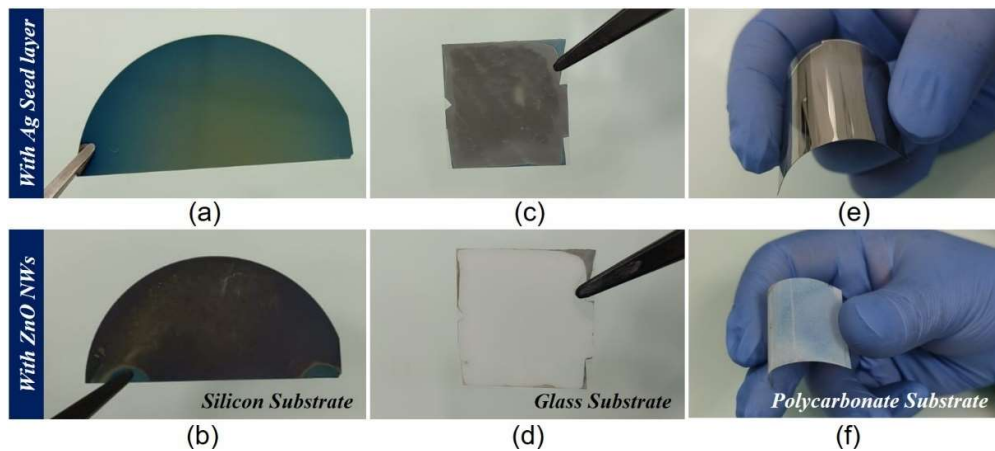


Figure 2.13: Photographs taken before and after the uniform and efficient growth of ZnO NWs on (a, b) silicon, (c, d) glass, and (e, f) flexible polycarbonate (PC) substrate

Furthermore, these optimized operating parameters were used to grow ZnO NWs on different substrates, demonstrating efficient uniform growth (see Figure 2.13). From the experimental and statistical model, it was estimated that in order to obtain high aspect ratio NWs, precursor concentration should be as low as 15 mM, growth temperature should be maintained at 95°C and growth time at higher values, i.e. 60 min. Further, ANNs can undergo iterative experimentation to refine the alignment between predetermined NW characteristics and observed experimental data. Neurons in ANNs are typically trained using large input datasets, especially in applications like data mining. However, the results show that ANNs can accurately predict NW characteristics, such as length and diameter, even with relatively small experimental datasets, validating the model's reliability.

Over the past decades, ZnO NWs have typically been grown using high-temperature seed sintering on rigid substrates, with numerous studies highlighting the impact of various growth parameters. However, the development of flexible electronics, which use substrates that cannot endure high-temperature sintering, has changed how these parameters affect NW growth. Consequently, metal-assisted synthesis methods that bypass the need for high-temperature sintering have become increasingly popular. Despite this progress, there remains a gap in understanding the growth mechanisms and the effects of various growth parameters on ZnO NWs on flexible substrates. For example, Gao et al. developed a method to synthesize well-aligned ZnO NWs on flexible polyimide (Gao et al., 2013). By studying the growth of NWs, on they found that the morphology of the NW arrays could be controlled by adjusting parameters such as ZnO seed layer thickness (50 to 400 nm), precursor ratio (1:1 to 1:4), and growth temperature (70°C to 80°C). The results showed that different thicknesses of the ZnO seed layer affected the morphology of the NWs. For instance, ZnO NWs on a 50 nm seed layer had a diameter of about 60 nm and a density of 100/ μm^2 , while those on a 100 nm seed layer had a diameter of 120 nm and a density of 50/ μm^2 . This indicates that thicker seed layers lead to larger diameters and lower densities of NWs. The precursor ratio also influenced the growth of ZnO NWs. An increased ratio resulted in larger, more uniform, and denser NW arrays. Additionally, the growth temperature played a crucial role. Increasing the temperature from 70°C to 80°C, while keeping other parameters constant, led to a gradual increase in the diameter of the NWs. Similarly, Justeau et al. compared Au, ZnO, and Al-doped ZnO (AZO) seed layers for the growth of ZnO NWs aimed at piezoelectric nanogenerator applications (Justeau et al., 2019). The results demonstrated that different seed layers significantly impacted the morphology of the ZnO NWs. SEM images showed that ZnO and AZO seed layers produced well-aligned ZnO NWs with hexagonal faces, high density, and perpendicular orientation to the substrate. In contrast, ZnO NWs grown on Au seed layers were randomly oriented. This indicates that ZnO and AZO seed layers strongly promote the aligned growth of ZnO NWs. Additionally, XRD patterns revealed that ZnO NWs grown on Au seed layers had relatively low (002) peak intensity compared to those grown on ZnO and AZO seed layers, suggesting that ZnO and AZO provide better piezoelectric performance than Au. Additionally, Yoo et al. developed a method for fabricating conformal ZnO NWs at low temperatures on flexible substrates using a solution processible metal seed assisted hydrothermal crystallization technique (Yoo et al., 2020). In this approach, an Ag ink solution is first coated onto a flexible plastic substrate and then reduced to form a nanoporous Ag layer at 130°C. The study demonstrated that growing ZnO NWs on Ag-seeded PC substrates requires at least 6 to 9 hours for complete development. However, the high temperature and prolonged growth time can alter the properties of the substrate. Therefore, a more systematic approach is needed, focusing on lower temperatures and shorter growth times. Utilizing advanced statistical and machine learning models as predictive tools can help develop a detailed growth diagram of ZnO NWs, enhancing the fabrication of flexible nanodevices.

2.1.4 Summary

The study investigated the impact of diverse CBD growth parameters, including precursor concentration, growth time, and growth temperature, on the morphological properties of the resulting ZnO NWs. With this work, we tried to understand the effect of various growth

parameters on a metal seeded substrate for the uniform growth of ZnO NWs. Prediction of accurate values at nanometer scale is near to impossible but approximate values of these parameters can always be estimated. This work is an attempt to estimate the optimized value to achieve high aspect ratio ZnO NWs with the synergies of experiments and statistical analysis using both RSM and ANN models. The ANN approach was employed to train the model, while the RSM technique was utilized to assess the interplay between operational parameters. Through a series of 20 randomized experiments, a second-order polynomial equation was effectively fitted to the above-mentioned growth parameters, with diameter and length of NWs as the responses. The R^2 values derived from RSM for both diameter and length were 0.94, respectively. Additionally, the ANN model yielded R^2 values of 0.92 for diameter and 0.96 for length. Furthermore, the role of Ag seeding in the growth of ZnO NWs was extensively elucidated. This technique presents an alternative avenue for establishing electrical connections among aligned ZnO NWs, offering promising prospects for electronic nanodevice applications.

2.2 FLEXIBLE HYBRID NANOSTRUCTURED CHEMIRERESISTIVE SENSING PLATFORM FOR LOW-TEMPERATURE TRACE HYDROGEN DETECTION

In this study, a cost-effective approach has been used to fabricate a flexible hybrid nanostructured platform on polyethylene terephthalate (PET) substrate incorporating a combination of zinc oxide (ZnO), titanium oxide (TiO_2), and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). This platform has undergone meticulous morphological characterization and comprehensive evaluation for H_2 gas sensing applications at both room temperature and 50°C .

2.2.1 Introduction

In the past several decades, the utility of gaseous hydrogen (H_2) has proliferated across a myriad of research and industrial applications. H_2 has emerged as a pivotal fuel source in the domain of space exploration, where it facilitates thermal management processes integral to spacecraft operations (Davoodabadi et al., 2021; Frischauf, 2016). Additionally, H_2 has found widespread adoption in the metallurgical industry, where it is leveraged for the thermal processing of metallic substrates. Furthermore, the semiconductor manufacturing sector has extensively integrated hydrogen as a crucial process gas for specialized device fabrication (Luong et al., 2021). Technological breakthroughs in hydrogen storage capabilities have increased hydrogen's potential as an eco-sustainable alternative to fossil fuels in automobiles. However, because of its properties such as flammability, colourlessness, and odorlessness, H_2 poses a serious hazardous condition in these scenarios. To ensure safety, it is necessary to fabricate highly sensitive, reliable, and cost-effective gas sensors that can detect H_2 at concentrations below the lower flammability limit of 4 vol% in air (X. Tian et al., 2015). As the H_2 economy grows, there is a greater need for research on novel H_2 sensors that can detect trace amounts of H_2 at low temperatures without the need for expensive power sources or compatibility with microelectronic integrated circuits. Although conventional H_2 detectors such as mass spectrometers, gas chromatographs, etc., have proven to be effective, however, they frequently have size, cost, and response time limitations (Sun et al., 2012). Furthermore, they may require high temperatures to function. As a result, H_2 gas sensors that are more compact, cost-effective, responsive, and can operate at lower temperatures are required (Gao et al., 2022; Liu et al., 2022).

As one of the highly researched sensing materials, Zinc oxide (ZnO) is a highly promising sensing material for gas sensing devices, especially for detecting H_2 ; however, its sensitivity as a bulk material is insufficient (Agarwal et al., 2021; Franco et al., 2022). In contrast, 1D ZnO nanostructures possess a large surface area and are suitable for use with other nanodevices due to their exceptional mechanical and thermal stability (Lupan et al., 2008b). Pristine ZnO nanostructures may have limitations in terms of the sensing performance of H_2 devices (Gupta et al., 2014). Therefore, previously published articles focus on the formation of metal oxide

heterostructures to improve the sensitivity and selectivity of a gas sensor. Hereinto, titanium dioxide (TiO₂), emerges as a highly stable n-type semiconducting material with exceptional optical, and electrical characteristics (Tian et al., 2021). Among the other heterostructure materials, TiO₂/ZnO combination emerges to be the most popular as one, here one oxide may result in providing high selectivity, while another oxide may enhance selectivity by, minimizing the response to interfering gases. For instance, Ramgir et al. developed a NO₂ gas sensor using TiO₂/ZnO hybrid nanowires (NWs) (Ramgir et al., 2020). The hybrid NWs demonstrated a fast response/recovery to 5 ppm NO₂ with a response of ~7% at 200°C. Similarly, Hashemi et al. used both electrospinning and hydrothermal methods to produce ZnO NWs on TiO₂/ZnO nanofibers (NFs) for selective detection of ethanol gas (Hashemi et al., 2020). The result demonstrates that the prepared NFs exhibited ~three times improvement with response/recovery to 10-200 ppm of ethanol gas under UV irradiation. The TiO₂/ZnO composite, despite its potential, continues to face challenges including sluggish response times, limited detection ranges, and low or inadequate sensitivity at room temperature. To overcome these limitations, the incorporation of a conductive polymer in the composite presents a promising solution for room-temperature chemiresistive sensors that offer improved sensitivity and faster response times (Farea et al., 2022; Shiu et al., 2022). Unlike conventional polymers used as insulators and dielectrics material, conducting polymers have alternating single and double bonds on their backbone that facilitate charge transport through extended π -conjugation (Xie et al., 2023a). For instance, poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) displays adjustable conductivity, excellent thermal stability. Additionally, it enhances room temperature sensing performance by promoting better charge transport and increasing the active surface area for gas adsorption (Khasim et al., 2021a; Pasha et al., 2019). To meet the demands of advanced applications that require high sensitivity and selectivity, it is crucial to develop a ternary composite that effectively leverages the strengths of each component. This combination can result in a more efficient, selective, and sensitive hydrogen gas sensor, particularly well-suited for operation at low temperatures.

Herein, we aim to develop an affordable technique for fabricating a next generation advanced flexible sensor that can detect ultralow H₂ gas at low temperatures. This platform was developed through the systematic growth of long and thin ZnO NWs on a flexible substrate using metal seeded growth, without requiring traditional high-temperature seed sintering methods. The platform also features a uniform deposition of TiO₂ NPs and PEDOT:PSS conductive layers, which combine to develop a versatile platform for H₂ detection. To the best of our knowledge, there have been no prior reports of the development of an ultralow flexible H₂ sensor that operates at low temperatures and consists of metal-seeded ZnO NWs and a unique ternary nanocomposite. This sensing platform delivers impressive performance, including high sensitivity, rapid response and recovery times, long-term stability, repeatability, and an extremely low LOD of 9 ppt. Given its excellent characteristics, this flexible sensing platform could potentially serve as a promising solution for both research and industrial applications that require stable, flexible, and sensitivity sensor.

2.2.2 Experimental Section

A polyethylene terephthalate (PET) substrate is purchased from France. The ZnO NWs were grown using hexamethylenetetramine (HMTA; (CH₂)₆N₄), zinc acetate, (ZnAc; Zn(CH₃CO₂)₂), isopropyl alcohol (IPA), which were purchased from Sigma Aldrich. Similarly, for the preparation of ternary nanocomposite, reagents such as TiO₂ as a thermal evaporation target source and a 1.3 wt% aqueous dispersion of conductive poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) in H₂O was also purchased from Sigma Aldrich.

(a) Preparation of Sensing Film on Flexible Substrate

Prior to the growth of ZnO NWs on a flexible PET (thickness: 100 μ m) substrate undergoes a standard cleaning protocol that involves the use of IPA, ethanol, and DI water to remove surface

contaminants. The optimized growth of ZnO NWs was initiated by depositing a thin layer of silver (Ag) onto the PET substrate via a thermal evaporation instrument (ME300 evaporator from PLASSYS, France). This was followed by the oxidation of the Ag layer in UV and O₃ exposure (Jolight Company Inc, USA) for 5 min. In a parallel process, a 35 mM ZnO growth solution consisting of a 1:1 ratio of ZnAc and HMTA in DI water is prepared and transferred to a round flask in a chemical bath deposition setup equipped with a PID controller (Fisher Scientific; UK). The Ag oxidized substrate was then carefully immersed in the prepared growth solution for 60 min at 85°C. The detailed variations of growth parameters for synthesizing ZnO NWs on PET substrate are presented in our separate study (Kadiri et al., 2014). After the growth process was completed, the samples are cooled, washed twice with DI water, and dried using a nitrogen gun to obtain ZnO NWs on PET substrate (named: ZTP1).

The E-beam evaporation system (EVAP MEB400 from PLASSYS, France) was used to further deposit 10 nm of TiO₂ nanoparticles (NPs) on ZTP-1 under the vacuum pressure (chamber) of 1.6×10^{-6} mbar. The bottom of the vacuum chamber contains the heater evaporator, and target source materials (TiO₂), were placed in a graphite crucible and provided joule heating to bring it to the required temperature to melt the source material (TiO₂). This energy resulted in the evaporation and deposition of TiO₂ on ZnO NWs grown PET substrate (named: ZTP-2). The ternary nanocomposite (named: ZTP-3) platform was further prepared by coating of conducting polymer (PEDOT:PSS) layer on the TiO₂/ZnO NWs substrate via spin coating technique. 1 mL of 1.3 wt% PEDOT:PSS solution was spin coated on TiO₂/ZnO NWs decorated PET substrate at a spinning rate of 1500 rpm for 60 sec to prepare the ZTP-3 device (see Figure 2.14).

(b) Device Fabrication and Gas Sensing Setup

The gas sensing instrumentation comprises of a mass flow controller (MFC), target gas tank, digital multimeter (Keithley Instruments), data acquiring system, and a power supply (see Figure 2.15). The preparation of final device involves the deposition of interdigitated electrodes (IDEs) on top of flexible functional platforms (ZTP 1-3) using a thermal evaporation system with a shadow mask that contains twelve 30/400 nm Ti/Al fingers, each with a length of 500 μ m, a width of 200 μ m, and a spacing between figures of 150 μ m. To measure the changes in resistance of the prepared sensor under varying concentrations of H₂ gas, a constant voltage of 1 V was applied to these IDEs, which were connected to a source measuring unit. A vacuum pump was also used to remove contaminated air from the sensing chamber. Further for selectivity measurements, we have taken 1% target gases (H₂, CH₄, and CO₂), balanced with 99% Argon (Ar). For NH₃ gas, we have perched dry 1% NH₃ cylinder balanced with 99% Ar. The response (%) of the devices was calculated by taking the ratio of the change in resistance before exposure (R_a) to the change in resistance after exposure (R_g), as expressed in the equation 2.8.

$$Response(\%) = \left| \frac{R_g - R_a}{R_a} \right| \times 100\% \quad (2.8)$$

Further, the gas sensor's performance is also dependent on the response and recovery time, which is measured as the amount of time it takes for the device to reach a 90% change in resistance after turning the H₂ gas on or off, respectively (Duan et al., 2022; Y. Guo et al., 2023). Additionally, humidity measurements are conducted to evaluate the sensor's response under varying relative humidity (RH%) conditions. To generate and control humidity in a gas sensing chamber, a mixer (mixing chamber) is used that combines dry air (zero air) with a regulated flow of water vapor. Dry air, which is free of moisture and contaminants, was introduced into the mixing chamber via a mass flow controller. Simultaneously, water vapor was produced using a water vapor bubbler. The flow of water vapor was meticulously regulated by N₂ gas flow in the bubbler to achieve the desired humidity level. The zero air and water vapor are mixed in a mixing chamber to ensure even distribution before being directed into the sensing chamber. A humidity sensor within the main gas sensing chamber continuously monitors RH%. Throughout the humidity test, the temperature of the gas sensing system was maintained at a constant 50°C.

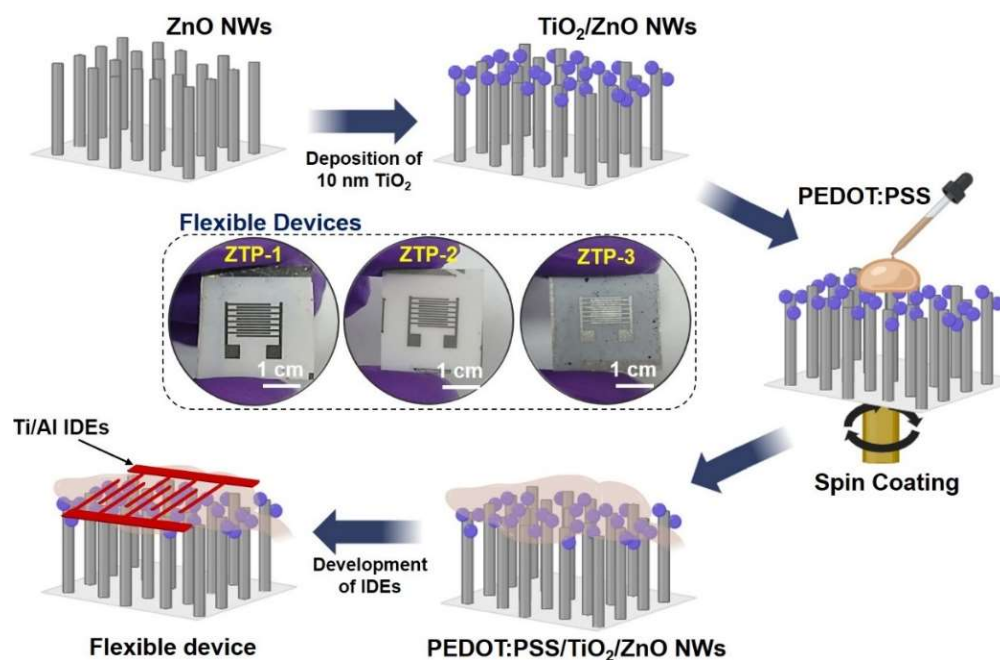


Figure 2.14: Schematic representation of the steps involved in the preparation of all three devices, along with an inset photograph of the fabricated flexible devices (showing ZnO nanowires with a diameter of ~ 350 nm and length of ~ 1.35 μm , TiO_2 nanoparticles of ~ 10 nm, and a PEDOT:PSS polymer layer of ~ 400 nm thickness)

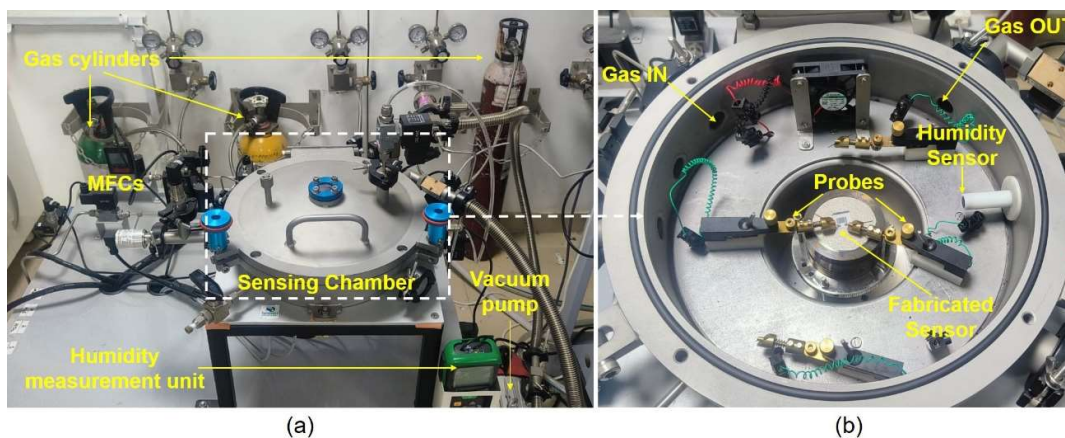


Figure 2.15: (a, b) Actual photograph of gas sensing instrumentation

2.2.3 Results and Discussion

(a) Structural and Morphological Characterization of Ternary Nanocomposite

Figure 2.16 (a) shows a FESEM image and a photograph of ZnO NWs. The image further illustrates that the PET surface was decorated with densely populated ZnO NWs. Upon closer inspection at higher magnification, the ZnO NWs exhibit a smooth surface with a hexagonal wurtzite structure, having diameters and lengths of ~ 350 nm and ~ 1.35 μm , respectively (see Figure 2.16 (d)). The growth mechanism of ZnO NWs, assisted by Ag, was due to the interaction between the oxidized Ag surface and ZnO precursors in the solution. The Ag_2O layer generated by UV and O_3 treatment of the ionized Ag surface attracts negatively charged Zn ion complexes present in the OH^- rich precursor solution, facilitating ZnO nucleation on the Ag_2O substrate (Geng et al., 2020). The presence of a lattice mismatch between the Ag_2O and ZnO result in a significantly increased energy barrier for heterogeneous nucleation (Tong et al., 2006).

Figure 2.16 (b) presents both a FESEM image and a photograph depicting TiO_2/ZnO NWs. The hybrid NWs exhibit a structural resemblance to pristine ZnO NWs, densely populating the

substrate. Upon closer examination via higher magnification scanning, no significant variation in NW diameter is visible, attributable to the thermal deposition of 10 nm TiO_2 NPs (see Figure 2.16 (e)). However, more detailed imaging reveals the uniform coverage of ZnO NWs with tiny NPs, imparting a visibly rougher texture to the overall NW surface compared to pristine NWs. This observation strongly suggests the establishment of a heterojunction between the two semiconductor materials. Additionally, XRD analysis supports the presence and significance of TiO_2 NPs. Figures 2.16 (c) and 2.16 (f) exhibit both lower and higher magnification images of the ternary nanocomposite, achieved through the coating of a PEDOT:PSS layer onto the TiO_2/ZnO hybrid NWs. As depicted, the polymer PEDOT:PSS, characterized by its long-chain structure, deeply permeates the TiO_2/ZnO hybrid NWs, thus uniformly decorating the NWs and giving rise to an enhanced nanotextured structure (see inset of Figure 2.16 (f)). The elemental composition and mapping of all the synthesized hybrid platforms are further performed to analyze the purity of synthesized nanomaterials. Additionally, Figures 2.16 (g) and 2.16 (h) display the EDS analysis and mapping of PEDOT:PSS/ TiO_2/ZnO NWs are presented, revealing a well-coated PEDOT:PSS layer on each individual hybrid NW. This is evidenced by the uniform distribution of carbon (C), oxygen (O), and sulfur (S) elements, along with zinc (Zn) and titanium (Ti), within the PEDOT:PSS/ TiO_2/ZnO NWs.

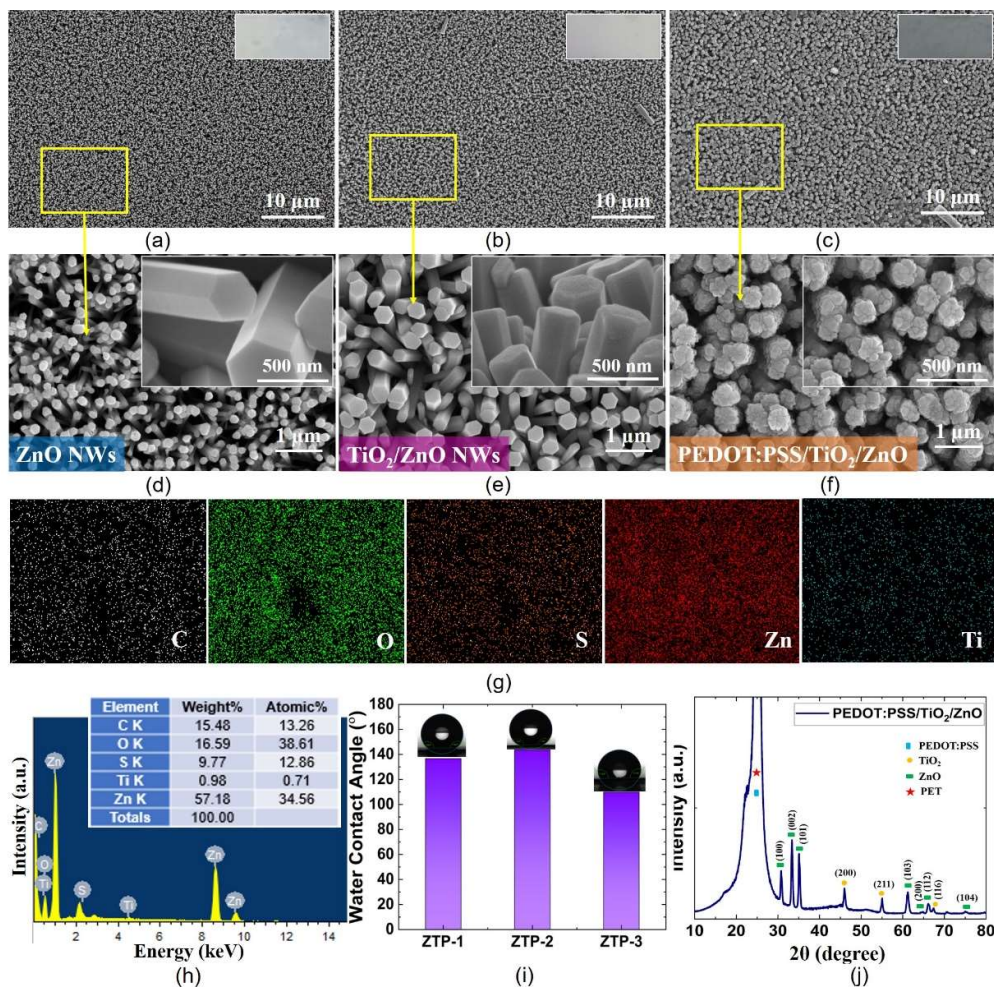


Figure 2.15: (a-f) FESEM images of the prepared ZnO NWs, TiO_2/ZnO NWs and PEDOT:PSS/ TiO_2/ZnO NWs, with inset showing the higher magnified images of the respective materials, (g-h) Elemental mapping and EDS of PEDOT:PSS/ TiO_2/ZnO NWs, (i) Contact angle (CA) results of prepared flexible platforms, and (j) XRD of PEDOT:PSS/ TiO_2/ZnO NWs

Moreover, the formation of hybrid NWs profoundly influenced the wettability of the resulting platform (see Figure 2.16 (i)). Pristine ZnO NWs exhibited a contact angle (CA) of 136.6° ,

whereas the TiO_2/ZnO nanostructures showed a higher CA of 143.5° . The pristine ZnO NWs exhibited hydrophobic characteristics. This was attributed to the synthesis process, which creates a ZnO surface with roughness, facilitating the manifestation of the "lotus effect". Deposition of TiO_2 onto the ZnO NWs further improved the surface roughness of the hierarchical TiO_2/ZnO structure, thus leading to an increase in hydrophobicity. However, the PEDOT:PSS/ TiO_2/ZnO composite exhibits a CA of 109.9° . This could be attributed to the inclusion of PEDOT:PSS within ZTP-3, resulting in a substantial number of hydrophilic sulfonic acid groups (Xie et al., 2023b). Figure 2.16 (j) shows the XRD patterns of PEDOT:PSS/ TiO_2/ZnO NWs, which were recorded at room temperature, covering a 2θ range from 20° to 80° using Cu K α 1 radiation with a wavelength of $1.54059 \text{ \AA}$. The predominant peak for the PET substrate appears at $2\theta = 26^\circ$, which was consistent with prior observations by Faraj et al. (Faraj and Ibrahim, 2011). Additionally, the XRD analysis successfully identified characteristic peaks attributed to the hexagonal wurtzite structure of ZnO and anatase TiO_2 , which demonstrates good relevance to the standard JCPDS 36-1451 (Mousa et al., 2021) and JCPDS 21-1272 (Molla et al., 2017) data file. The XRD pattern shows strong diffraction peaks, indicating that both ZnO and TiO_2 have high crystallinity. Yan et al. reported a large peak for PEDOT:PSS spanning 15° to 30° (Yan et al., 2014). These peaks, however, were hidden in the ZTP-3 sample by the strong PET peak overlaid on the PEDOT:PSS signal (Shiu et al., 2022). Furthermore, peaks at 31.8° (100), 34.4° (002), 36.3° (101), 62.9° (103), and 66.4° (200) represent ZnO, while peaks at 48.1° (200), 55.1° (211), and 68.8° (116) correspond to TiO_2 .

(b) Gas Sensing Results

I-V characteristics of fabricated flexible devices were investigated at 1 V. The conductivity of the device increased with the formation of TiO_2/ZnO heterostructure and PEDOT:PSS/ TiO_2/ZnO NWs based ternary nanocomposite at ambient temperature which indicates the ohmic nature of the electrical contact of devices (see Figure 2.18 (a)). At 100 ppm ZTP-1 started to show a non-stable response at H_2 gas. Further, the addition of TiO_2 in the ZTP-1 device resulted in the detection of H_2 gas at RT. With changes in the concentration level of H_2 gas, the electrical resistance of the ZTP-2 device increased. However, the device shows drift in response, which affects the recovery of the sensor at the baseline after the exposure to H_2 gas. The sensor showed relative response of $\sim 10\%$ at 100 ppb and gradually increased to $\sim 34\%$ at 100 ppm. This behaviour of the device was because, at a low gas concentration, the surface interaction of H_2 molecules with the surface of the sensor was low, leading to a lower response. The sensitivity increased stepwise when the gas concentration increased to create an enhanced surface interaction, leading to a rising response at a higher concentration. Furthermore, the ZTP-3 device also shows a similar response as the ZTP-2 device, which implies that the addition of PEDOT:PSS doesn't have a significant response on the device performance at RT. The previously published article suggests that at room temperature, H_2 gas molecules partially interact with the surface absorbed oxygen molecules, resulting in a lower response. Whereas, at a higher temperature, the rate of reaction becomes higher and there is an increase in the oxygen ions on the sensor surface from the absorbed oxygen species responsible for the maximum response (Goutham et al., 2018; X. Liu et al., 2023).

With the increased temperature at 50°C , all the devices demonstrate good stability and reversibility as shown in Figure 2.17, as the resistance decreases rapidly and returns to its original value under the exposure of different concentrations of H_2 gas. The ZTP-1 devices demonstrated a response of 23.05% to 34.59% under the exposure of 0.1 to 100 ppm of H_2 gas. At RT, the ZTP-2 exhibited a relative response of $\sim 10\%$ at 100 ppb, which improves 2.5 times with the increase in temperature to 50°C , thus reaching 25.87% at 100 ppb. However, the ZTP-2 devices show 11.9% and 2.8% higher response at 100 ppb and 100 ppm, respectively as compared to ZTP-1 devices at 50°C . Previous studies have shown that creating heterostructures by combining different MO_x materials can enhance gas sensitivity at higher temperatures (Panigrahi et al., 2024). This is achieved by introducing more electron depletion layers (EDL), altering the energy band structure, increasing adsorption sites, or improving the catalytic activity of the materials. With the

introduction of conducting polymer in the MO_x heterostructure resulted in the enhanced response of the ZTP-3 device.

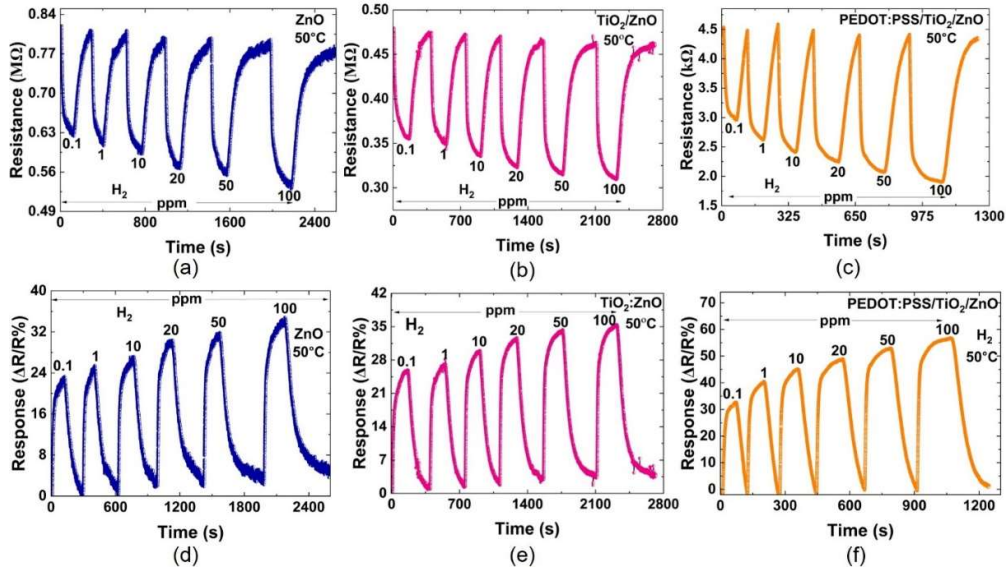


Figure 2.16: (a, c, e) Time-dependent resistance curves and (b, d, f) Corresponding time-dependent response (%) curves for ZTP 1-3 devices at 50°C, showcasing responses to different concentrations of H_2 gas

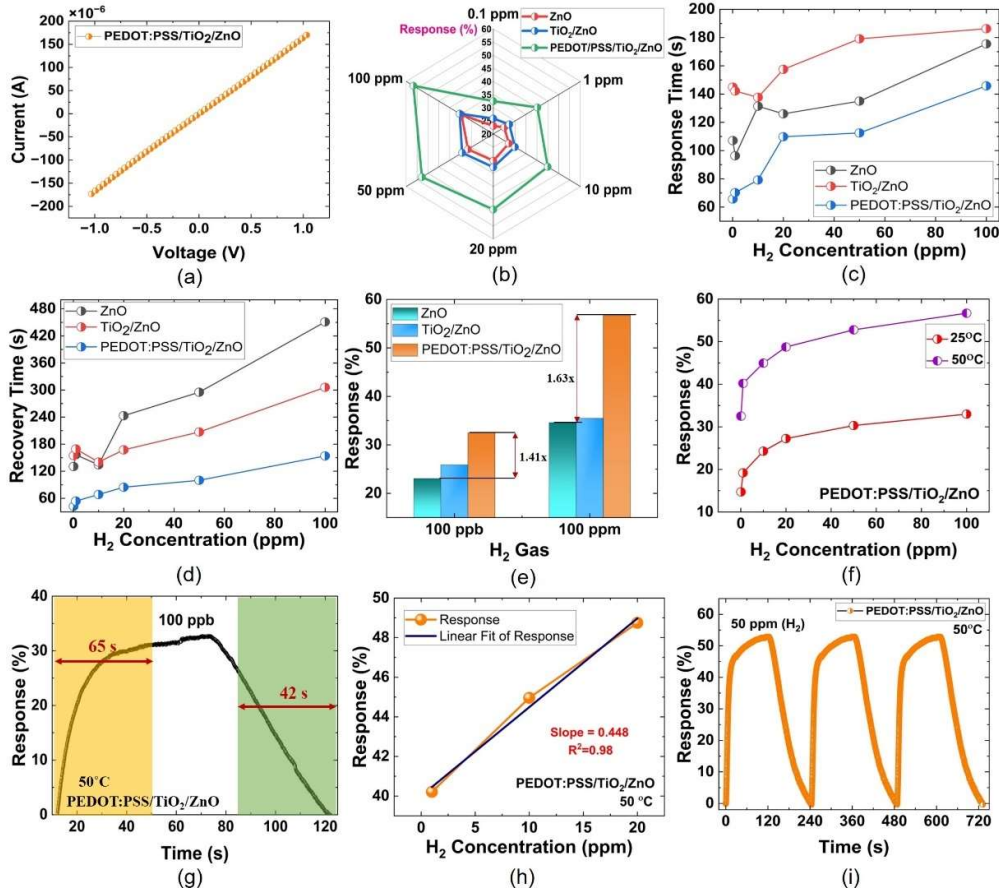


Figure 2.17: (a) I-V Curve of ZTP-3 device, (b) Radar plot depicting the response (%) vs concentration curve for H_2 gas across all devices at 50°C, (c, d) Response and recovery times plot vs H_2 concentration of all devices at 50°C, (e) Comparative response of all devices at 100 ppb and 100 ppm H_2 gas at 50°C, (f) Comparative analysis of the response of ZTP-3 device at RT and 50°C, (g) Response of ZTP-3 device for 100 ppb H_2 gas at 50°C, including

response and recovery time, (h) Linear regression analysis for sensitivity calculation based on response, and (i) Three-cycle repeatability test conducted at 50 ppm H_2

Figure 2.18 (b) illustrates the radar plot for comparative response (%) of devices (ZTP 1-3). The results highlight the superior response of the ZTP-3 device at each H_2 gas concentration. Additionally, Figure 2.18 (c, d) displays the response and recovery times of all devices for H_2 gas concentrations ranging from 0.1 to 100 ppm. The result demonstrates that the ZTP-3 device shows fast response and recovery times in comparison to other devices. Further, the ZTP-3 device shows 1.41x (141% higher response by proportion) and 1.63x (163% higher response by proportion) at 50°C compared to the ZTP-1 device (see Figure 2.18 (e)). Figure 2.18 (f) shows the comparative graph of the ZTP-3 device at 25°C and 50°C, the results demonstrated the higher response of the device at 50°C. This sensing behavior of the ZTP-3 device is due to the greater availability of H_2 molecules at higher concentrations at higher temperatures, resulting in an effective reaction of H_2 molecules with the enhanced active sites of ternary nanocomposite. As a result, as the gas concentration increases, the response shows an increasing trend. Figure 2.18 (g) illustrates the response of the device to a concentration of 100 ppb of H_2 . At a temperature of 50°C, the sensor exhibits a response of 32.51%, with response and recovery times of 65 sec and 42 sec, respectively. Moreover, sensitivity is determined by the change in response for every 1 ppm variation in the target gas concentration (Duong et al., 2021). This is represented by the slope of the linear regression line in Figure 2.18 (h), which is calculated to be 0.448% ppm⁻¹. Utilizing this slope, the sensor's LOD is calculated for ZTP-3 sensor, resulting in an ultralow LOD of ~9 ppt. Notably, this LOD meets the requirement for trace level measurement, underscoring the sensor's high sensitivity and precision.

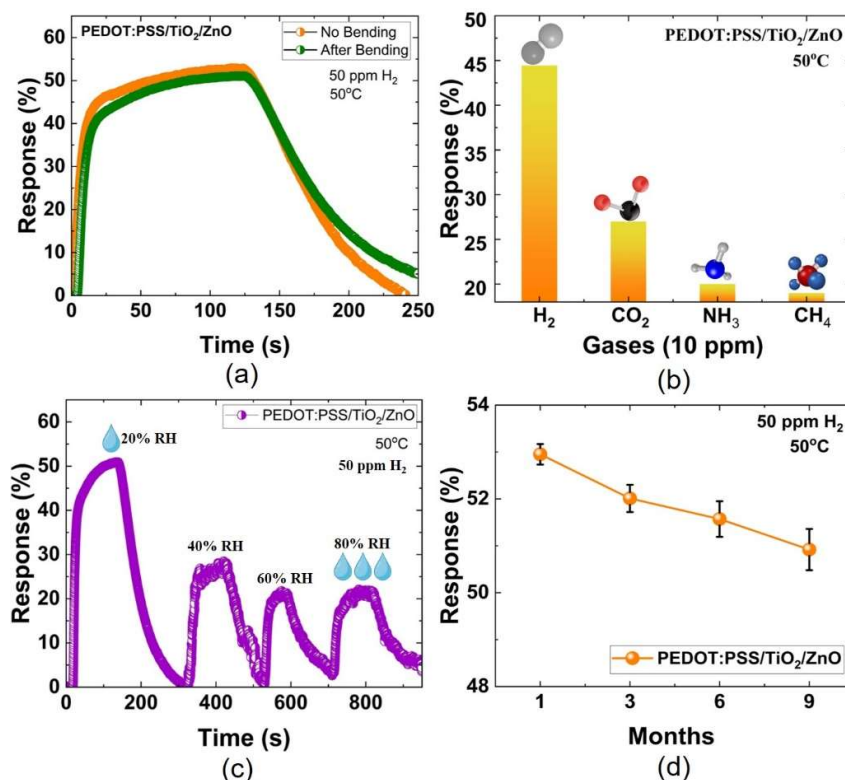


Figure 2.18: (a) Comparative analysis of the ZTP-3 sensor's response before and after bending, (b) Selectivity test results at 50°C, (c) Response of sensor in varying RH%, and (d) Long term stability results

To evaluate the practicality of the prepared flexible devices, the sensing performance of the ZTP-3 sensor was evaluated in terms of its repeatability, bendability, selectivity, and long term stability. To assess the consistency of the sensor's output, a repeatability study was carried out on the ZTP-3 device for H_2 gas as shown in Figure 2.18 (i). The experiment revealed that the

device's response was almost uniform throughout the three-cycle test at 50 ppm H₂ gas concentration. These findings indicate that the device is stable and can be utilized in practical settings. As depicted in Figure 2.19 (a), the effectiveness of the sensor was evaluated using a 50 ppm H₂ gas before and after bending. Post bending, the sensor's response showed a negligible decrease in response at 50°C. This decline can be attributed to the mechanical stress imposed on the sensing layer during bending, which may alter the layer's morphology and orientation, disrupting the electrical connection between the sensing layers and electrodes, and resulting in reducing the response of the sensor. In actual use, low-temperature flexible devices must have the ability to distinguish between gases. The selectivity of the ZTP-3 sensor was examined in the presence of various interfering gases at 10 ppm (see Figure 2.19 (b)). The relative response percentages for CO₂, NH₃, and CH₄ were found to be ~27%, ~20%, and ~18%, respectively. These values are significantly lower than the response to H₂ (44.96%) at 10 ppm. Among the other interfering gases investigated, H₂ was found to be a strong reducing agent that efficiently removed the adsorbed oxygen present on the surface of the ZTP-3 device, resulting in high selectivity. To enhance the assessment of sensor performance, it is essential to test ZTP-3 under varying relative humidity (RH) levels. As depicted in Figure 2.19 (c), the ZTP-3 sensors demonstrated a change in response (%) to 50 ppm H₂ at 20-80% RH. The ZTP-3 sensor exhibited a decrease in response as the RH increased continuously. This trend became saturated at RH levels greater than 60%. This behavior can be attributed to microstructural changes of PEDOT:PSS film present in the ZTP-3 sensor, which is also supported in the literature (Taccola et al., 2013). Typically, PEDOT:PSS has a granular structure with conductive PEDOT⁺ rich grains encased by hydrophilic and insulating PSS⁻ chains. Upon moisture adsorption, the polymeric chains of PSS⁻ swell, disrupting the connections between the conductive PEDOT⁺ segments and causing a change in electrical resistance. Furthermore, the strong dipole moment of water molecules can shield the conductive sites within the PEDOT⁺ rich regions, further reducing the conductivity (Popov et al., 2019). Literature shows that at 60% RH, a water meniscus layer forms on the PEDOT:PSS surface due to temporary saturation moisture adsorption. Further, at higher humidity levels (80% RH), the PEDOT:PSS film is anticipated to display hydrogel-like stability in sensing applications and can revert to its original dry state after losing water (Xie et al., 2023b). Furthermore, Figure 2.19 (d) depicts a long-term stability of the ZTP-3 sensor for 9 months, which demonstrated that the sensor exhibited negligible variation in response (%) when subjected to 50 ppm H₂ gas at a temperature of 50°C. These results indicate that the device is well-suited for a wide range of applications, including environmental, industrial, and domestic settings. Moreover, the comparative analysis of previously developed flexible devices with low temperature H₂ gas detection is shown in Table 2.8.

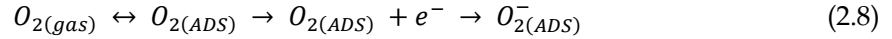
Table 2.8: A comparative analysis of recently developed flexible devices for room/low temperature H₂ gas detection

Flexible devices	H ₂ gas	Temperature (°C)	Response time (s)	Recovery time (s)	Response (%)	LOD
Pd/SnO ₂ on PI (Ren et al., 2023)	30 ppm	25	~1000	~1000	70	250 ppb
CNT/Pd Ripstop fabric (McConnell et al., 2020)	8.5 mol%	-	~306	-	~85	0.1 mol%
PEDOT:PSS/Pd fabric (Zhu et al., 2021)	4%	25	19	73	31.6	-
Pd/WS ₂ fabric on PI (Kuru et al., 2016)	5%	25	119	370	7.8	10 ppm
rGO/SnO ₂ /PVDF (Punetha et al., 2020)	100 ppm	25	34	142	49.2	500 ppb
Pd/ZnO on PI (Rashid et al., 2013)	1000 ppm	25	19	-	91.2	200 ppb
Pd/PAN NFs (Jiang et al., 2019)	25 ppm	70	-	-	12.2	-

ZnO/Sb ₂ O ₃ (Pradeep et al., 2021)	3000 ppm	100	400	475	~2.9	-
PEDOT:PSS/TiO ₂ /ZnO (This work)	100 ppb	25	97	114	14.71	1 ppb
	100 ppb	50	65	42	32.51	9 ppt

(c) Sensing Mechanisms

The prepared ternary nanocomposite demonstrates a good response to H₂ at low temperature due to its chemical composition, morphological structure, and gas adsorption on the surface of composite material. Figure 2.20 presents the schematic and energy band diagram for the possible sensing mechanisms. When ZnO is exposed to air, oxygen molecules from the air chemically adsorb on the ZnO surface, which leads to the trapping of electrons from the conduction band (CB) of ZnO. This results in the generation of O₂⁻ (<100°C) and the development of an EDL due to the decrease in electron density (equation 2.8). The decrease in the conductivity of the electrons is a result of the decreased electron density. In response to exposure to H₂ gas, these oxygen ions react with the gas molecules, leading to the release of electrons back into the CB of ZnO. This results in a decrease in the EDL and a decrease in resistivity. However, when exposed to normal ambient conditions, water molecules on the surface of ZnO NWs desorb, leading to the regain of their initial resistance (equation 2.9).



Moreover, Figure 2.17 (b, e) illustrates the enhanced response of TiO₂/ZnO NWs to H₂ gas subsequent to TiO₂ deposition, contrasting with the performance of pristine ZnO NWs. The improved sensing properties to H₂ gas in this case are due to two reasons. First, the TiO₂ decoration enhanced the O₂ adsorption by increasing the number of active sites on the material surface, which enhanced the gas surface reactions. Second, due to the formation of n-n junctions between ZnO NWs and TiO₂ NPs (Yu et al., 2019). When TiO₂ comes into contact with ZnO, a transfer of electrons from TiO₂ to ZnO will occur, causing a band bending around the surface due to the large gradient of the band gap and work function (Ying Yang et al., 2009). This results in electron depletion and further bends the energy band, leading to a higher resistance in the sensing material compared to the pristine ZnO sensor. The capture of electrons occurs in both ZnO and TiO₂ near their interface (Zou et al., 2016). This results in the formation of a depletion layer and a potential barrier at the ZnO-TiO₂ interface. When ZnO/TiO₂ nanostructures are formed, the depletion of electrons in ZnO is greatly increased due to the formation of n-type heterojunctions in addition to the adsorption of oxygen molecules (Deng et al., 2013).

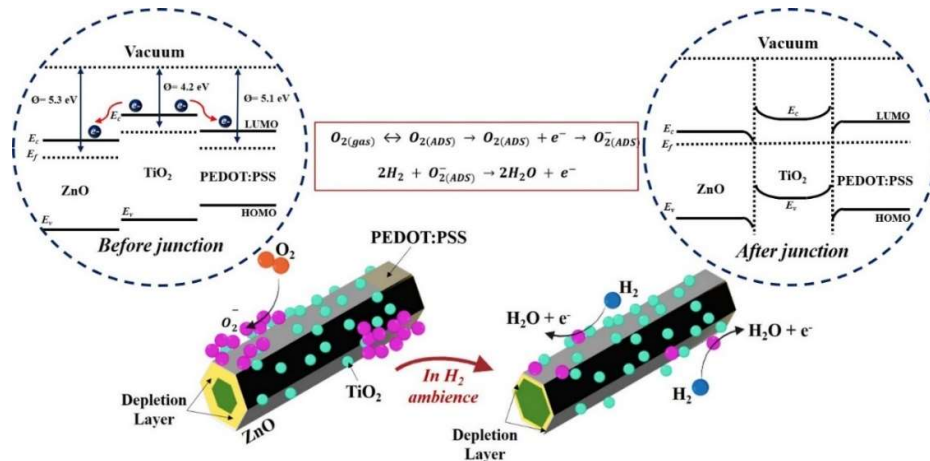


Figure 2.20: Schematic and energy band diagram of PEDOT:PSS/TiO₂/ZnO based flexible gas sensor

Further, the incorporation of a PEDOT:PSS layer onto the TiO₂/ZnO hybrid NWs has resulted in an enhancement of the sensing response to H₂ gas, as shown in Figure 2.18 (b). Previous research has reported the work functions of PEDOT:PSS, TiO₂, ZnO as 5.03, 4.2, and 5.1 eV, respectively (Choi et al., 2020; Figueroa et al., 2019). The improved gas sensing response of the composite can be attributed to the formation of a p-n heterojunction between the p-type PEDOT:PSS and the n-type TiO₂/ZnO composites. The π electrons in PEDOT:PSS affect the charge transfer induced by H₂, resulting in the formation of a neutral backbone in the polymer chain due to a reduced amount of charge carriers. This reduction in charge carriers leads to decreased electrical conductivity (Khasim et al., 2021b). Furthermore, the rise in resistance observed may be attributed to the diffusion of gas molecules within the polymer matrix. Each PSS chain interacts electrostatically with several shorter PEDOT chains in the PEDOT:PSS layer, giving it a unique structure (Seekaew et al., 2014; Tseng et al., 2023). This closer proximity of PSS chain molecules facilitates the hopping of charge carriers between the PEDOT chains. The hindrance of gas molecule chemisorption inhibits the movement of charge carriers over shorter distances, thereby raising the resistance with an increase in H₂ gas concentration (Zhu et al., 2021). Through the synergistic effect among the ternary nanocomposites, a sensitive response to H₂ is achieved at a lower temperature.

2.2.4 Summary

This study presents the fabrication of a flexible hybrid nanostructured platform combining ZnO, TiO₂, and PEDOT:PSS nanomaterials. The ternary nanocomposite sensor, comprising PEDOT:PSS/TiO₂/ZnO hybrid NWs, exhibits a significant improvement in detecting trace levels of H₂ gas at low temperatures. Significantly, the relative response of the pristine ZnO NWs sensor reached ~34.58%. This response surged to ~56.69% upon the incorporation of TiO₂ and PEDOT:PSS into the ternary nanocomposite-based sensor for 100 ppm H₂ concentration at 50°C. Furthermore, the ternary nanocomposite-based sensor demonstrates selectivity towards H₂ over CO₂, NH₃, and CH₄, achieving a LOD of ~9 ppt. These findings highlight the potential of the developed hybrid nanostructured platform and ternary nanocomposite-based device for monitoring trace levels of H₂ gas, particularly in industrial applications. This study lays the foundation for future researchers aiming to design highly sensitive, selective, and efficient flexible H₂ gas sensors, which are crucial for environmental remediation, low level gas detection, and monitoring.

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