Chapter-4

PTB7 Decorated ZnO Nanorod-Based Room Temperature Ammonia Gas Sensor

The Part of the work is adopted from-

J. S. Rana, S. Das, and S. Jit, "**PTB7 Decorated ZnO-Nanorod-Based Room-Temperature Ammonia Gas Sensor**," ***IEEE Sens. J.***, vol. 22, no. 23, pp. 22398–22403, Dec. 2022, doi: 10.1109/JSEN.2022.3213366.

4.1 Introduction

The photodetection properties of the PTB7-based horizontal and vertical devices are explored in Chapter 2 and Chapter 3, respectively. The performance parameters of the PTB7-based photodetectors are excellent. Like many other organic semiconducting polymers, PTB7 can also investigated for room temperature gas sensing applications with excellent selectivity because it does not require temperature elevation like metal oxide-based gas sensors during operation. Therefore, the present chapter is dedicated to the PTB7-based two-terminal device for ammonia gas sensing at room temperature.

Ammonia is an essential chemical for nitrogen-based fertilizers, pharmaceuticals, cleaning products, explosives, refrigeration, dairy and ice cream plants, wineries and breweries, petrochemical facilities, fruit and vegetable juices, and soft drink processing facilities [41], [87], [137]. Ammonia is also projected as an energy storage medium for sustainable energy due to its higher hydrogen content than hydrogen (H_2) itself in the same volume [138]. However, excess exposure to ammonia gas has catastrophic impacts on human health [139]. According to the Occupational Safety and Health Administration (OSHA), the maximum limit of exposure for a human being is 25 ppm for 8 hours and 35 ppm for 10 minutes [41]. Exceeding this limit may result in blindness, lung damage, coma, and death [89][140]. Thus, it is very important to detect, monitor, and maintain a safe level of ammonia gas concentration inside various industries and plants dealing with ammonia gas for their products. As a result, the development of gas sensors for ammonia detection is currently in great demand.

Metal oxides such as CuO, TiO_2, SnO_2, and ZnO as well as metal oxide composites with polymers such as P3HT, PBTTT, PQT-12 have been consistently explored by researchers for ammonia detection [42], [96], [141], [142]. However, the sensing devices need much more improved performance in terms of sensitivity,

selectivity, response time, etc. In the present chapter, the gas-sensing performance of PTB7 as an active layer over the base layer of ZnO nanorods is investigated for ammonia sensing. The experimental procedure for the fabrication of the PTB7-based ammonia gas sensor is presented in section 4.2. Later, the results and discussion are included in section 4.3. The summary of the chapter is provided in the section 4.4.

4.2 Experimental Details

4.2.1. Material Preparation and Device Fabrication

All the materials and chemicals were provided from Sigma-Aldrich, and Merck Millipore. Since the chemicals were purchased with standard purity grade, hence, no further purification was carried out before use. For device fabrication two FTO coated glass samples of size 1.5×1.5 cm were cleaned using wet cleaning procedure with soap solution, acetone, iso-propanol followed by deionized (DI) water rinse after each step. ZnO seed layer was used for ZnO nanorods synthesis by hydrothermal method. 0.1M solution of zinc acetate dihydrate was prepared in 2-methoxyethanol by stirring the solution for 120 minutes at 60 °C [22][23]. Then 0.5 ml Diethanolamine (DEA) was dropwise added to stabilize the solution till it became transparent. The solution was aged for 24 hours at room temperature before spin coating for stabilization of the nanoclusters formed in solution after continuous stirring [24]. This prepared solution was then spin-coated @1500 rpm on a cleaned FTO substrate for 30 sec. The sample was then dried @150 °C for 30 min. after spin coating the seed layer solution. Subsequently, the sample was immersed in an equimolar solution of hexamethylenetetramine (0.01 M) and zinc nitrate dehydrate (0.01M) in an autoclave at 90 °C in closed furnace for 3 hours. Next, the sample was taken out from autoclave, and rinsed rigorously with DI water followed by annealing at 400 °C about 45 minutes to achieve the ZnO nanorods.

The polymer PTB7 (3mg/ml) was dissolved in chloroform and stirred for 6 hours at 60 °C. Then 20 µL PTB7 solution was used for spin coating on ZnO nanorods at 2000 rpm for 45 sec. The substrate was then dried for 10 min at 110 °C. Finally, the Ag electrodes (of ~120 nm thickness) in the interdigitated pattern were fabricated by the shadow mask technique using thermal evaporation method (HIND HIVAC Vacuum Coating Unit Model-BL-300). The interdigitated finger length of 6 mm and the spacing between the fingers of 0.2 mm in the mask were used for electrode deposition. Various fabrication steps followed for the proposed device structure are summarized in **Figure 4.1.**

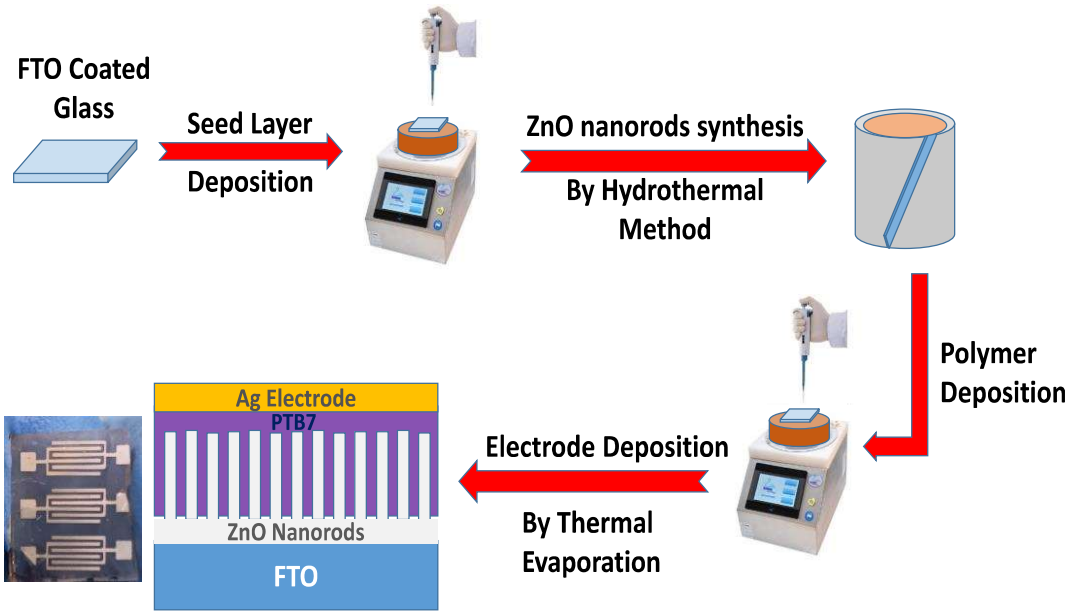

Figure 4.1 Hydrothermal method of ZnO nanorods synthesis.

4.2.2. Device Characterization and Measurement Setup

The sensing performance of as-fabricated device was measured in a custom-built laboratory gas sensing setup as shown in **Figure 4.2**. We used a homemade 10 liter gas chamber made of stainless steel for our measurements. All of the studies were carried out in dark conditions at room temperature (~25 °C) in a gas sensing chamber with a

controlled atmosphere to test the device's real-time functionality. The relative humidity (RH) was measured as 75% during the characterisation. The relative humidity inside the gas chamber was maintained by a bubbler and vacuum pump connected to the sensing chamber. The NH_3 gas was injected from gas cylinders through mass flow controller (MFC) into the chamber in measured quantity. The electrical characterizations of the device were done in a semiconductor parameter analyzer (Keysight, model B1500A).

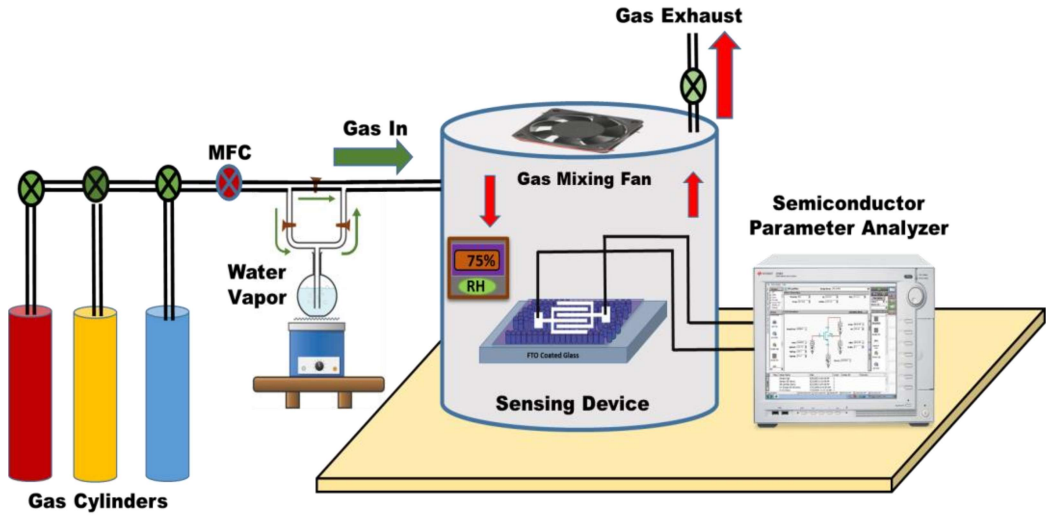

Figure 4.2 In-house developed gas sensing setup.

4.3 Results and Discussion

4.3.1. Thin Film Characterization

The X-Ray Diffraction (XRD) spectrum of the ZnO nanorod film is shown in **Figure 4.3**. The peaks at (110), (002), (101), (102), and (110) are well-matched with the wurtzite structure of the ZnO nanorods [25]–[30]. The high-resolution scanning electron microscopy (HRSEM) image of ZnO nanorods after polymer deposition has been examined by Nova Nano SEM 450 shown in **Figure 4.4 (a)**. The average length and diameter of the nanorods were found to be ~ (863 ± 100) nm and ~ (344 ± 21) nm, respectively. The average roughness, root mean square roughness, average peak-to-valley height of the ZnO layer were obtained as ~(175 ± 4) nm, ~(140 ± 5) nm, and ~(1276 ± 5)

nm respectively. Further, the maximum area peak height and maximum area valley depth of the ZnO nanorod layer were found to be ~(568 ± 3) nm and ~(708 ± 3) nm, respectively. The surface morphology is depicted in AFM image **Figure 4.4 (b)**. The polymer film on the ZnO nanorods behaves as capping over the nanorods confirmed in **Figure 4.4 (d)**. The average thickness of the polymer film is obtained as ~(30 ± 1.4) nm by thin film analyzer (Filmetrics F20-UV).

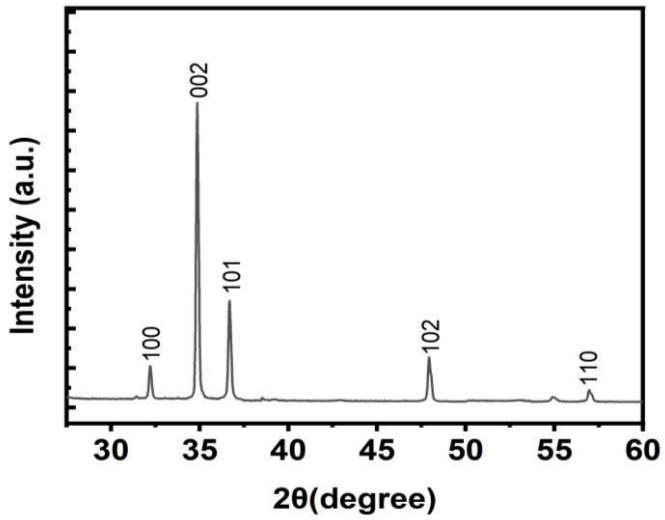

Figure 4.3 XRD of ZnO nanorods.

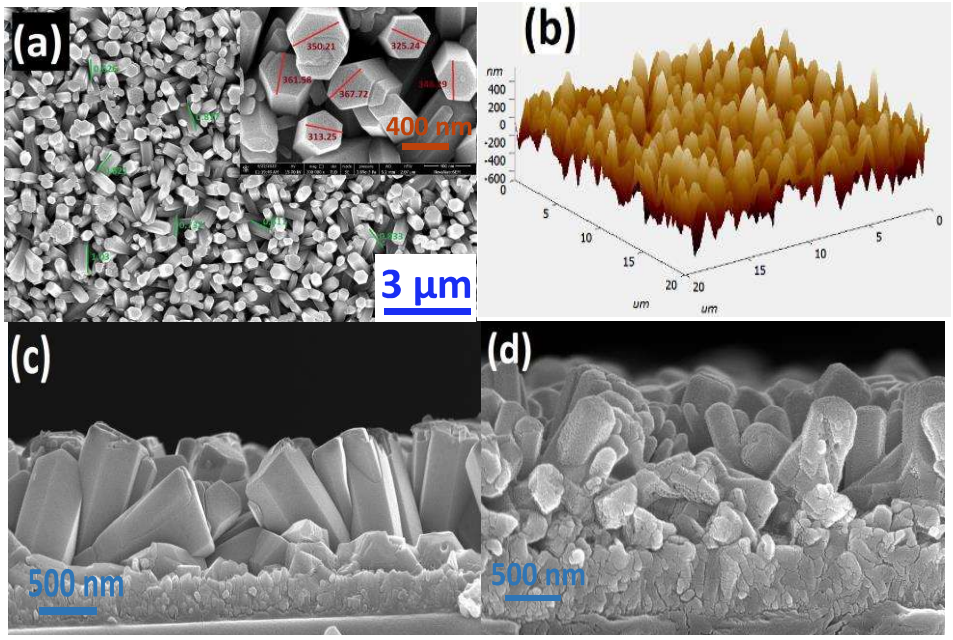

Figure 4.4 (a) High-resolution SEM image of PTB7 deposited ZnO nanorods with the HRSEM image of the ZnO nanorods in the inset, (b) 3-D AFM image of the polymer film on ZnO nanorods, (c) cross-sectional view of the pristine ZnO nanorods, and (d) cross-sectional view of the PTB7 decorated ZnO nanorods.

4.3.2. Gas Sensing of the device

The gas sensing characteristics of as-fabricated devices have been studied for -2 to 2 V with varying gas concentrations from 2 ppm to 50 ppm as shown in **Figure 4.5(a)**. It is also observed from **Figure 4.5(a)** that the response saturates above 2 V bias voltage in air. That is why we have restricted our measurements to -2 to 2 V bias voltage. This also gives the low-voltage operation capability of our proposed sensor. **Figure 4.5(a)** gives the ammonia gas response of the PTB7-ZnO NR of 66.92% at 20 ppm NH_3 at 2 V applied voltage. **Figure 4.5(b)** compares the response of the ZnO NR film device with and without PTB7 layer. It is observed that a gas response of only 15.56% is obtained at 20 ppm NH_3 concentration for the device without PTB7 layer. Clearly, the enhancement in response from 15.56% to 66.92% is obtained by the use of the PTB7 polymer on ZnO nanorods as confirmed by **Figure 4.6(b)**. This improvement can be attributed to the combined effects of the polymer roughness and large surface-to-volume ratio of the ZnO NRs.

The gas sensing response was calculated as following relation [14][15]:

$$S\,(\%) = \left|\frac{I_0 - I_g}{I_o}\right| \times 100 \tag{4.1}$$

where, I_g, I_0 are the current with gas exposure and current without gas exposure, respectively.

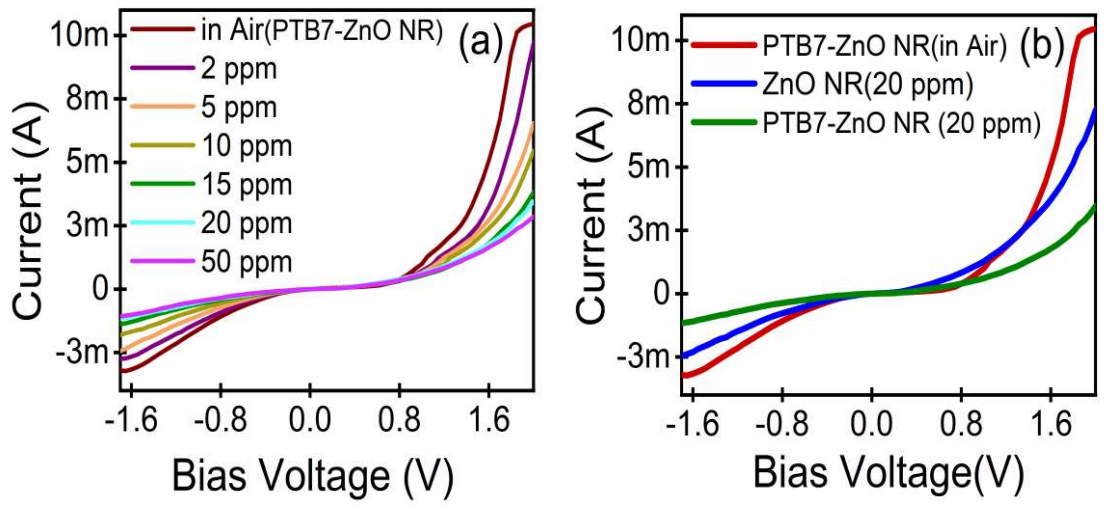

Figure 4.5 (a) Current-voltage characteristics of PTB7-ZnO NRs device with varying ammonia concentration. (b) comparison of the current-voltage characteristics of ZnO NR device with and without PTB7 layer under 20-ppm ammonia.

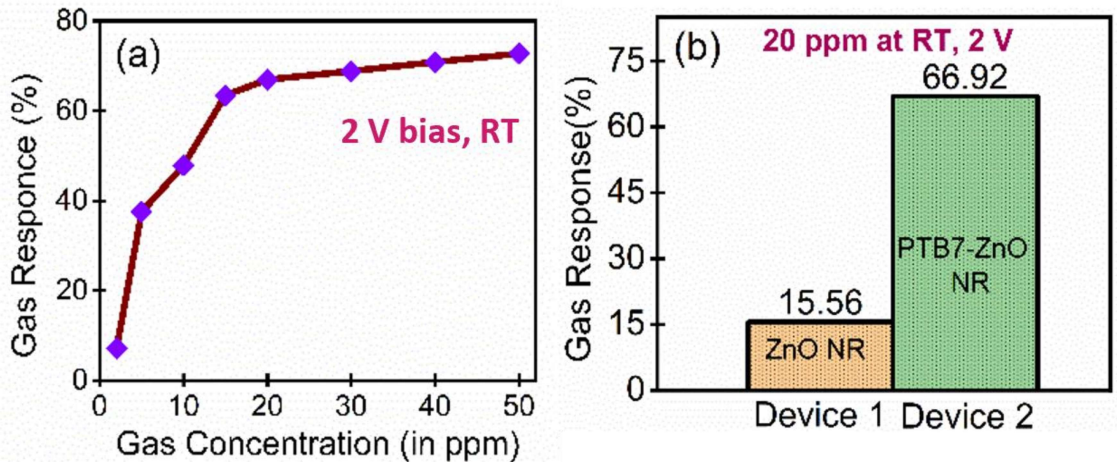

Figure 4.6 (a) Gas response of the PTB7-ZnO NR device with varying gas concentration from 2 ppm to 50 ppm at 2 V bias, (b) comparison of gas response of only ZnO NR device and PTB7-ZnO NR device at 20 ppm ammonia.

The gas response of the proposed PTB7-ZnO NR device is shown in **Figure 4.6(a)**. The maximum response of 72.72% is measured with 50 ppm. It is also observed from **Figure 4.6(a)** that the gas response of the proposed sensor increases almost linearly up to 15 ppm. However, the response becomes nearly saturated for NH_3 concentrations beyond 15 ppm.

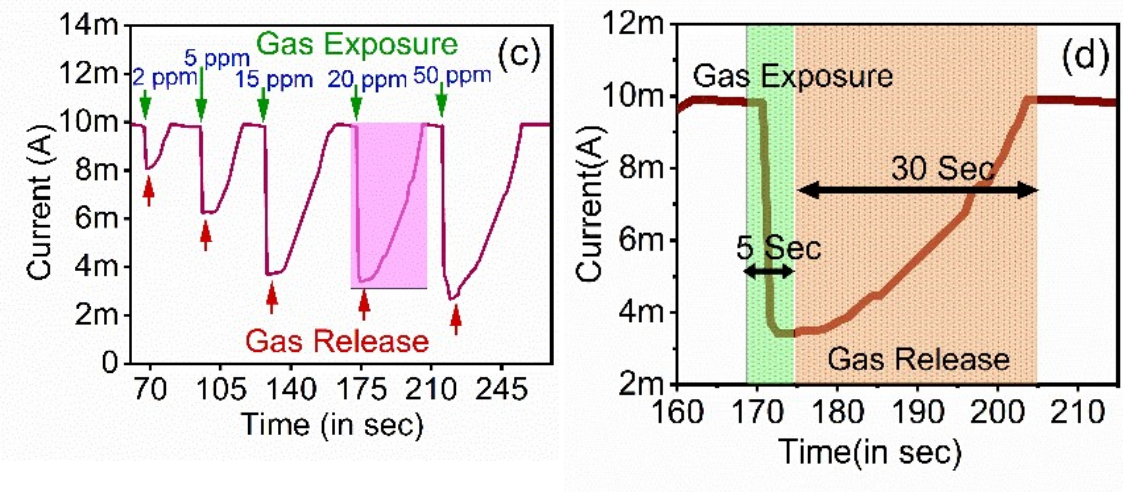

Figure 4.7 (a) Transient gas response characteristics of the proposed PTB7- ZnO NR device at 2 V for different concentrations of ammonia gas varying from 2 ppm to 50 ppm, (b) enlarged view of the transient gas response at 20 ppm for analyzing the response and recovery times.

The transient response of the proposed device under varying concentrations (2-50 ppm) of ammonia gas is shown in **Figure 4.7(a)**. The analysis of the response time (i.e. time required for changing the gas response of the device from 10% to 90% of its saturation value after exposing the device to the ammonia gas) and recovery time (i.e. time required to change the gas response from 90% to 10% of the saturation value after the ammonia gas is removed from the measuring unit) of the device at a fixed concentration 20 ppm shown in **Figure 4.7(b)** are 5 s and 30 s respectively. Since the gas response is nearly saturated above 20 ppm (**Figure 4.6(a)**), we have analyzed the transient response at only 20 ppm. However, our measurements show average response and recovery times of (5±0.49) s and (30±16) s for all gas concentrations varying from 2-20 ppm.

To test the robustness of the proposed device in a real environment, the gas response has been analyzed with different relative humidity from 75% to 30%. **Figure 4.8(a)** shows the variation of less than 10% in the response of the device. This confirms that the proposed device has a high tolerance to humidity. **Table 4.1** compares the performance parameters of the proposed ammonia sensor with other polymer-based ammonia sensors reported in the literature. The proposed device shows low-concentration sensitivity, high

room-temperature response, high tolerance to humidity and fast response time. The performance parameters of the proposed device are very much encouraging for ammonia gas sensing and monitoring applications in various industries dealing with the manufacturing, processing and transportation of ammonia gas.

4.3.3. Selectivity and Stability

The selectivity of the gas sensor has been investigated by exposing acetone, methanol, ethanol and nitrogen oxide of known concentrations in the gas-sensing measurement chamber under identical conditions. The response to various gases is shown in **Figure 4.8(b)**. Our proposed device shows the highest sensitivity to ammonia at much lower concentration than that of other gases under consideration. This confirms high selectivity of the device to the ammonia.

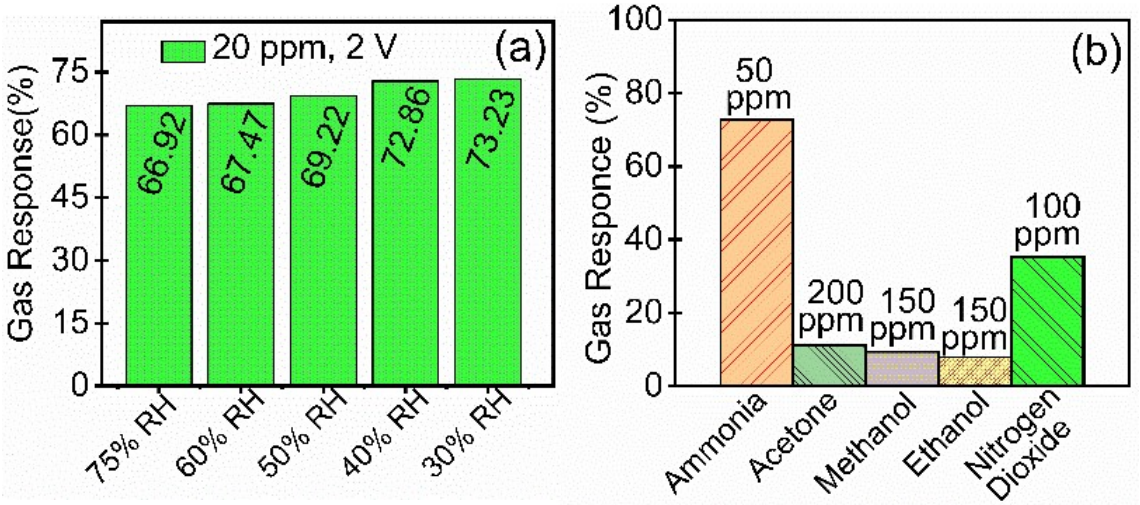

Figure 4.8 (a) Gas response analysis for different values of relative humidity, (b) selectivity analysis of the proposed device.

It is important to mention here that the fabrication and characterization of the proposed ammonia sensor have been carried out in normal atmospheric conditions without using any clean room/controlled environment. Since the performance of any unpackaged polymer-based device is degraded with time due to changed atmospheric conditions, we have measured the gas response of the fabricated device over 7 weeks to analyze the stability of the device as shown in **Figure 4.9**. A change of nearly 10% in the

gas response is observed from the figure after 7 weeks. Thus, the proposed unpackaged device shows reasonably good stability in normal atmospheric conditions. However, the effect of environment on the performance parameters can be made negligible by using the proper packaging of the proposed device.

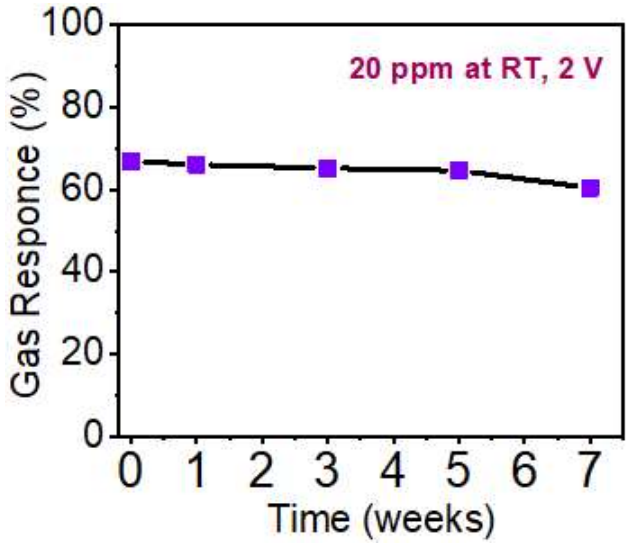

Figure 4.9 The stability study of the device over a 7-week period.

4.3.4. Comparison of Fabricated Device

The performance of the fabricated device is compared with the other fabricated ammonia gas sensors in below **Table 4.1**.

Table 4.1 Gas sensing performance of ammonia sensor

Device/Structure	Bias Voltage (in Volts)	Conc. of ammonia gas (in ppm)	Temperature (°C)	Gas Response (in %)	Response Time and Recovery Time	References
ZnO and p-Phenylenevinylene	---	10 ppm	RT	8.83%	9.8 s and 17.3 s	[143]
P3HT/MoS_2 Thin Film	10 to -60 volt	100 ppm	RT	63.45%	---	[45]
PQT-12/CdSe QD Composite	10 to -40 volt	100 ppm	RT	51%	65s and 240s	[104]
Pt NP/WO_3 Thin Film	-2 to 2 volt	1000 ppm	225 °C	72%	12 s and 75 s	[144]
Cu_2O-MoS_2 Microsphere	---	100 ppm	130 °C	43%	90 s and 100 s	[145]
MoS_2/CuO Heterojunction	-2 to 2 volt	100 ppm	RT	47%	17 s and 26 s	[146]

PQT -12 Thin Film	-5 to 5 volt	100 ppm	RT	8.6%	8 s and 103 s	[91]
ZnO-PANI Nanocomposite	---	20 ppm	RT	38.9%	35 s and 38 s	[147]
ZnO-rGO	---	50 ppm	RT	2.30%	68 s and 223 s	[148]
Pristine ZnO NR	-1 to 1 volt	100 ppm	650 °C	22.6%	8 s and 12 s	[149]
ZnO Thin Film	----	50 ppm	RT	1.2%	---	[150]
ZnO Nanorods	-2 to 2 volt	1000 ppm	300 °C	80.6%	< 3 min	[151]
ZnO NR	---	500 ppm	RT and 150 °C	8% and 60%	5 min and 20 min	[152]
ZnO NR and PTB7	-2 to 2 volt	20 ppm	RT	66.92%	5 s and 30 s	**This Work**

4.3.5. Ammonia Gas Sensing Mechanism

The as-fabricated sensing device's mechanism can be explicated by polymer interaction with ammonia. High surface-to-volume ratio of nanostructures offers a significant increment in the sensing response. PTB7 film coating over ZnO nanorods is working as nanorods of polymer resulting in a high sensing response at room temperature as confirmed by **Figure 4.4(d)**.

The gas sensing mechanism is explained with the help of doping/de-doping phenomenon at the sensing surface of the device as depicted in **Figure 4.10** [96][104][91]. Since PTB7 is a p-type polymer, it possesses many electron vacancies forming 'hole' carriers. Being a reducing agent, the lone pair electrons of ammonia molecules interact with PTB7 polymer to form a linkage-type structure as illustrated in **Figure 4.10(a)** [96][45]. In the analogy of semiconductor physics, NH_3 molecules act as donors to the p-type PTB7 polymer [153]. Thus, the hole density (and hence the conductivity) of the polymer is reduced after NH_3 adsorption [96]. The reduction in the conductivity (i.e. increase in resistivity) is observed from the reduction of current with the increased ammonia concentration shown in **Figure 4.5(a)**. On the other hand, the

reverse mechanism occurs during the desorption of the ammonia molecules [154]. The adsorption/desorption processes are shown in **Figure 4.10(b)**.

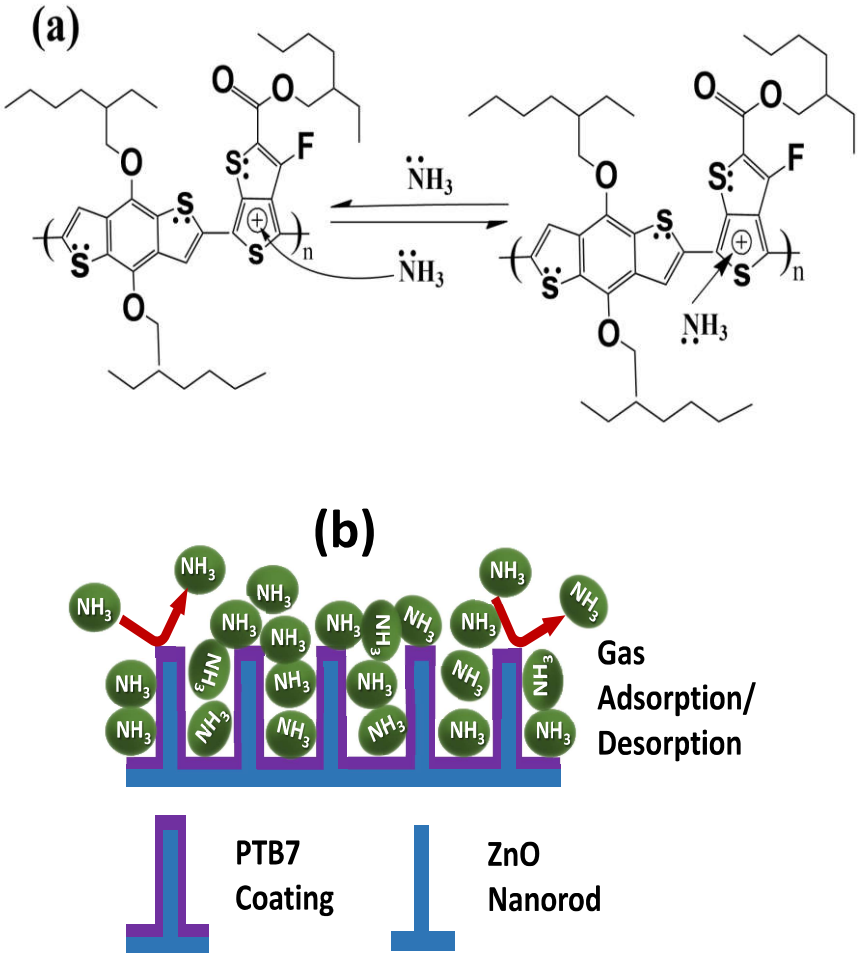

Figure 4.10 (a) Ammonia sensing mechanism, (b) adsorption and desorption of ammonia molecules on the surface of active layer.

4.4 Conclusion

A high-sensitive room temperature PTB7-ZnO NR based ammonia sensor has been fabricated as well as characterized at identical ambient conditions. The device shows the lowest room-temperature gas response of 7.12% at 2 ppm and the highest gas response of 72.72% at 50 ppm. The use of PTB7 on ZnO NRs improves the gas response of ZnO NR based ammonia sensor from 15.6% to 66.92% at 20 ppm ammonia. The proposed device shows a response time of 5 s and recovery time 30 s measured in the ambient

environment. The device is fabricated by an easy solution process and ZnO nanorods have been synthesized by a very well-established easy hydrothermal process. The proposed sensor is shown to detect low concentrations of ammonia at room temperature and low bias voltages below 2 V. The device is shown to have better gas response with shorter response/recovery time as compared to many reported metal oxides and nano-composites based ammonia sensors.