

Conductometric assisted ZnO and polypyrrole composite based NH₃ gas sensor

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Abstract

Metal oxides are excellent choices as base materials in emerging technologies in the field of Gas Sensors. In this work, an effort is made to prepare the ZnO and polypyrrole composite thin film using sol-gel technique. Nanocomposite thin film was prepared using spin coating on glass substrates for ammonia gas sensing. ZnO and polypyrrole sols were prepared using sol-gel technique and thin films were prepared by using spin coater. The nanocomposite thin films were prepared by varying the percentage composition of ZnO and Polypyrrole. Structural, optical and morphological properties of the prepared films were done using XRD, UV-Visible and SEM studies. The films were separately prepared on Inter-Digital Transducers for gas sensing applications. Gas sensing response characteristics of the prepared sensor were performed using laboratory. The sensing response of the prepared films is observed and found to be maximum (~33) for the 70%PPy+30%ZnO film at a relatively low operating temperature of about 150°C.

1. Introduction

Development of gas sensors is essential for the protection of environment and work places from harmful and hazardous gases [1]. Due to the increase in the emission of gases from automobiles, there is a sharp rise in air pollution. The alarming increase in the usage of various gases in day today life, either in a domestic kitchen or workplaces or industries especially of explosive or toxic nature has immensely increased the need for reliable gas sensors in the commercial market. The major attributes to look forward in a gas sensor are: (i) high sensing response, (ii) small recovery time, (iii) selectivity [2]. In the present work, focus has been done on the detection of ammonia (NH_3). This is because, NH_3 , in gaseous form is a highly harmful to human health, commonly produce as animals and human excreta at home, work places and industries in many ways [3, 4]. The lower limit of NH_3 perception by smell by human beings is around 5 ppm, thus, it is important to develop efficient gas sensors which can monitor and detect the low concentration of (smaller than ,5 ppm) NH_3 leaks [5]. Researchers have put enormous efforts on designing the highly efficient NH_3 gas sensors [6, 7].

Semiconductor metal oxides represent an interesting, and a varied class of materials that are suited for gas sensing applications for several types of gases like oxidizing gases, reducing gases, odorous gases etc.. Amongst the various metal oxides exploited for gas sensing, Zinc Oxide (ZnO) is the most suitable metal oxide for gas sensing applications having diverse semiconducting, piezoelectric and pyroelectric properties [8]. Conducting polymers is a new class of sensing material which have arisen interest in due to good electrical and optical properties [9]. Poly pyrrole (PPy) is mostly exploited material due to highly stable nature at high temperatures and ease in synthesis by using chemical methods [10]. Arora et al. have prepared PPy thin films electrochemically for NH_3 sensing in the concentrations of 0.01–1% [11]. Another report is on chemically synthesized Ppy films giving show response values 4–8% and response time of 4 min to detect NH_3 gas [12].

Nanocomposite thin films have found enormous applications in the field of gas sensing due to high sensing response at lower operating temperature and selectivity towards a target gas [13, 14]. Wu et al. have observed the improvement in selectivity towards the target NO_x gas by making the nanocomposites of ZnO and PPy prepared by the simple method of mechanical mixing [13]. Patil et al. designed a highly sensitive NO₂ gas sensor using ZnO and PPy nanocomposite thin films [14]. Wang et al. have proposed a highly novel sensing platform of nanofiber composites of PPy/TiO₂-ZnO for detecting a small concentration of NH₃ [15].

Hence, the present manuscript focusses on the development of NH₃ gas sensor using the composite thin films of ZnO and PPy by varying its compositional percentage.

2. Experimental Details

The nanocomposite thin films were prepared using sol-gel and spin coating technique. PPy nanoparticles were synthesized by using chemical polymerization method and ZnO nanoparticles were synthesized using sol-gel method. The ZnO composites with PPy were prepared by adding ZnO (NPs) in different weight ratios (20% and 30%) in smooth agate mortar and pestle. The nanocomposite powder was put in m-cresol and stirred for 11 h to get casting solution. Thin films were prepared on glass substrates by spin coating method at 3000 rpm for 40 s and dried on hot plate at 100°C for 10 min.

The prepared films were characterized structurally, optically and morphologically using XRD, UV-Visible and SEM techniques respectively. XRD measurements were done in θ -2 θ scan mode. For UV-Visible measurements, transmittance of the films was recorded as a function of wavelength. SEM studies were done in non-contact mode.

Gas sensing measurements were done using indigenously assembled laboratory setup. The films were separately prepared on Inter-digital Transducers for gas sensing measurements as shown in figure 1.

Platinum (Pt) Inter-Digital Electrodes were formed by using Photolithography on glass substrates. PPy and ZnO composite thin film was prepared on the Pt Inter-Digital Electrodes substrates. The system consist of a chamber in which vacuum is created using rotary pump. The sensing system is placed on a temperature-controlled stage and fixed concentration of gas is inserted inside the chamber. The variation in the resistance of the sensor is measured by the data acquisition system which is interfaced with computer. Selectivity measurements of the prepared sensor were also done by measuring the gas sensing response of the prepared sensor in the presence of the interfering agents. A fixed concentration of interfering agents is inserted inside the chamber and corresponding response was measured.

3. Results And Discussion

XRD pattern of ZnO thin film is shown in the inset of figure 2 which shows the perfect growth of highly c-axis oriented film. A well-defined and sharp peak is observed at 34.1° indicating the (002) plane [10].

Figure 2 shows the X-ray diffraction pattern of PPy and ZnO composite thin films by varying their composition. Both the XRD graphs show a broad peak at around 24.8° indicating their amorphous nature [11]. This broad peak may be attributed to the scattering offered by the PPy chains at the interplanar spacing [12].

The transmittance spectra of the composite thin films in UV-Visible regime is shown in Figure 3(a). This indicates that with increase in the concentration of ZnO, transmittance increases. The transmittance spectra is exploited to calculate the band gap of the prepared thin films using Tauc plot [16]. The variation of the square of the absorption coefficient with the energy (in eV) is shown in figure 3(b). The linear portion of the plot is extrapolated to cut the x-axis giving the value of band gap. The band gap increases minutely from 3.89 eV to 3.92 eV with increase in the percentage composition of ZnO from 20% to 30% [17, 18].

Morphological study of the film (70% PPy + 30% ZnO) is analyzed using Scanning Electron Microscopy technique (figure 4). The average grain size of the film is mentioned in the image is around 38 nm. The prepared film is found to be rough and porous appropriate for gas sensing applications [19].

The variation of response of the prepared sensing matrix to the target NH_3 gas is shown in figure 5. Both the sensing response of the prepared films (80%PPy + 20%ZnO and 70%PPy + 30%ZnO) shows maximum response at the operating temperature of 150°C . The sensing matrix having composition 70%PPy + 30%ZnO gives higher sensing response of 33 as compared to the other composition. This is attributed to the two factors: (i) higher band gap and (ii) higher surface roughness and porosity.

Figure 6 (a) shows the time variation response of 70%PPy + 30%ZnO sensor structure where a resistance in air is about $13.7\text{ M}\Omega$ and after the exposure of target NH_3 gas, the resistance decreases to $R_g = 2.15\text{ M}\Omega$ in about 100 s (response time). Recovery time of the sensor is about 50 s after removing the target gas from the chamber. Figure 2 (b) shows the repeatability of the prepared sensor at an operating temperature of 130°C towards the 100 ppm of NH_3 gas.

Figure 7 shows the response of 70%PPy+30%ZnO composite thin film structure towards other interfering harmful and toxic gases like liquefied petroleum gas (LPG), NO_2 , SO_2 and carbon dioxide at $T_{\text{opt}} = 150^\circ\text{C}$. The presently prepared gas sensor demonstrates poor response towards 100 ppm of these interfering gases as compared to that obtained for 50 ppm of NH_3 gas (Figure 7). This further indicates that the presently prepared gas sensor is highly selective towards the target NH_3 gas.

4. Conclusion

Summarizing the above work, an effort has been made to prepare the ZnO and Poly pyrrole composite thin film for the detection of NH_3 gas. ZnO and Poly pyrrole sols were prepared using sol-gel technique. Two types of films were prepared by varying the percentage composition of ZnO and PPy (80%PPy + 20%ZnO and 70%PPy + 30%ZnO). Nanocomposite thin film was prepared using spin coating on glass

substrates. Structural studies of the films were done using XRD which showed the amorphous nature of the prepared films. Band gap of the prepared films was also estimated using UV-Visible transmittance studies. Band gap of the film having composition 70%PPy + 30%ZnO was found to have higher band gap. Morphological study of this films was also done using SEM and showed the formation of highly rough and porous film. Gas sensing studies were also performed of the prepared films. A maximum sensing response of ~33 is obtained for ZnO/PPy nanocomposite thin film (70%PPy + 30%ZnO) at a relatively low operating temperature of about 150°C.

Declarations

Competing interests

The authors declare that they have no competing interests" in this section.

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Authors' contributions

APSG has devised the problem for the present work. All the literature survey and work plan of the present work has been done. Analysis of the performed work.

AP has done all the experimental work. Some part of the analysis of data has also been done

AK has done the final proofing of the article and reviewed the article for publication. Scientific inputs in the analysis of the data has also been given.

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Figures

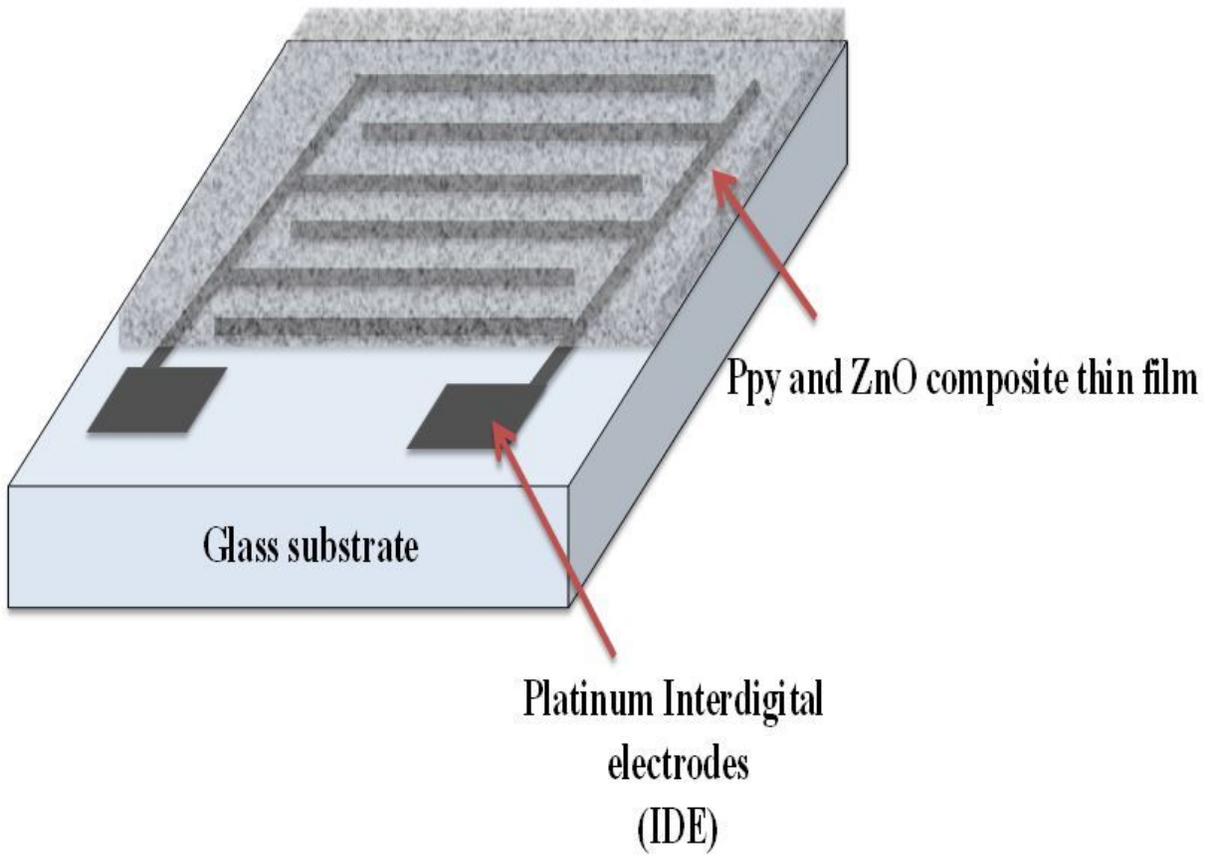


Figure 1

Schematic of sensor electrodes prepared for gas sensing applications

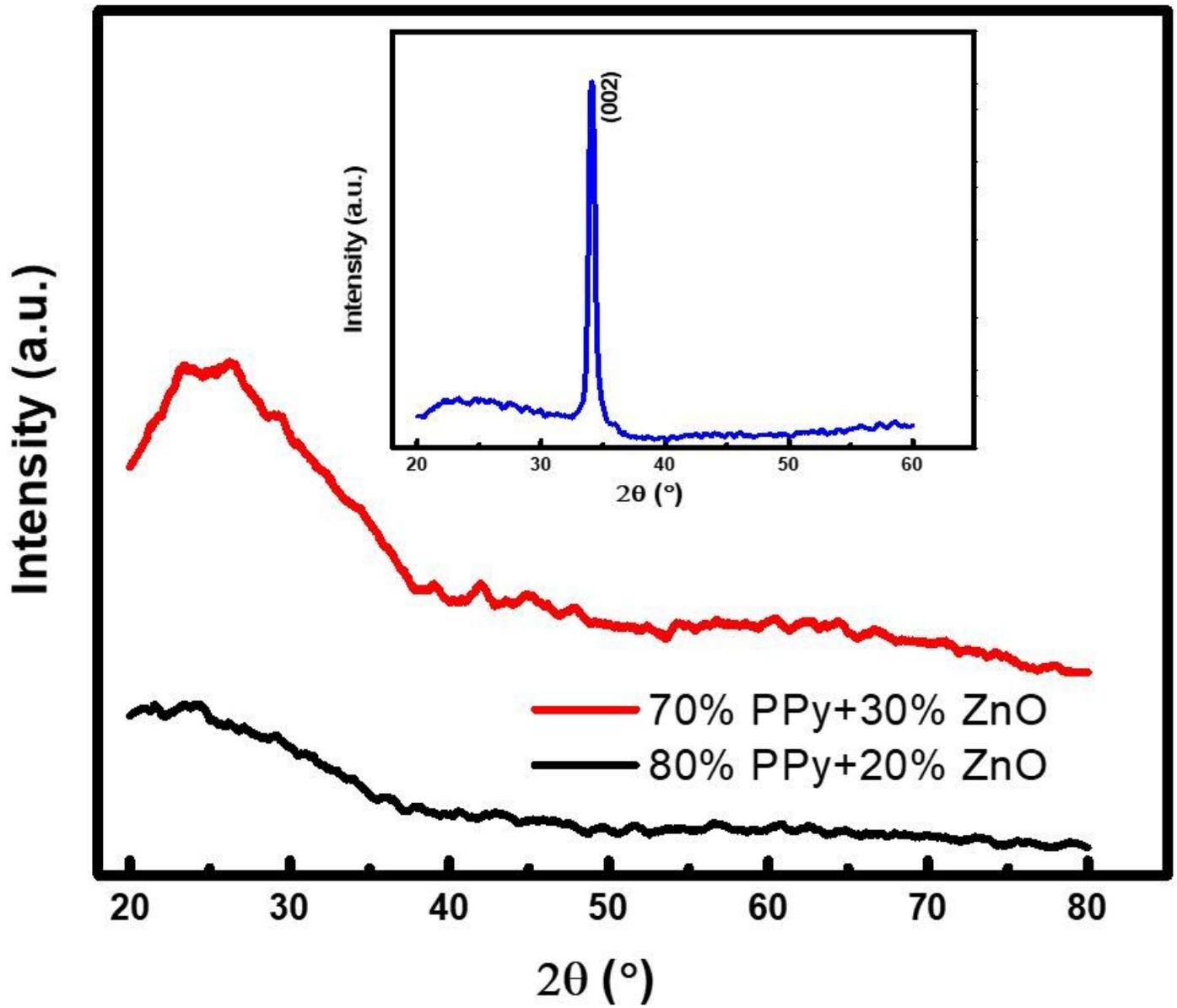
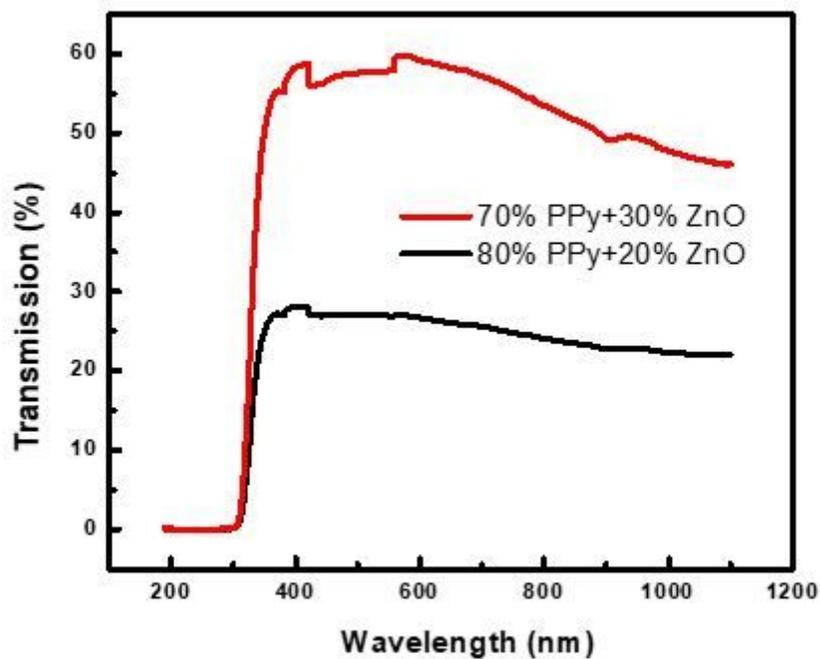
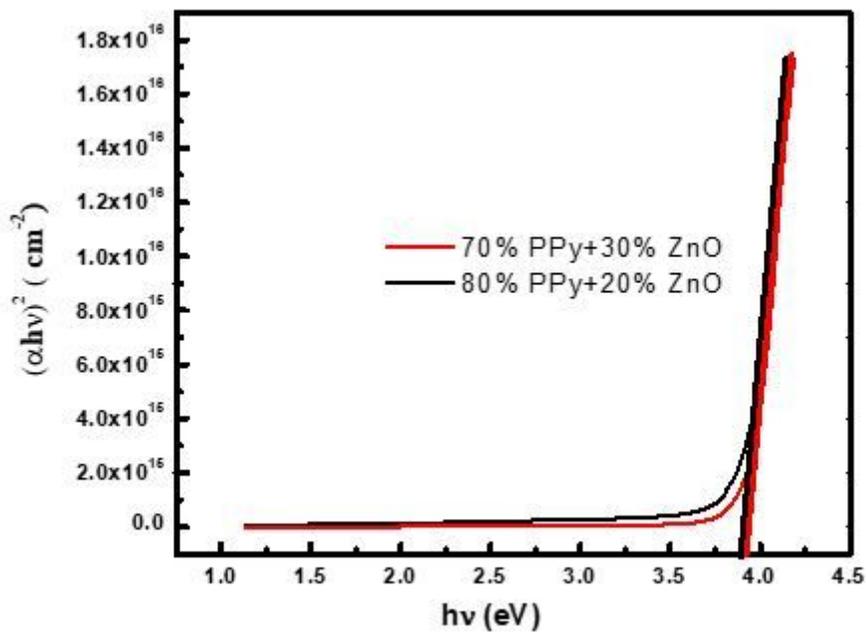


Figure 2

XRD spectra of the PPy and ZnO composite thin film



(a)



(b)

Figure 3

(a) Transmittance spectra of the films in UV-Visible regime, (b) Tauc plots to estimate the band gap

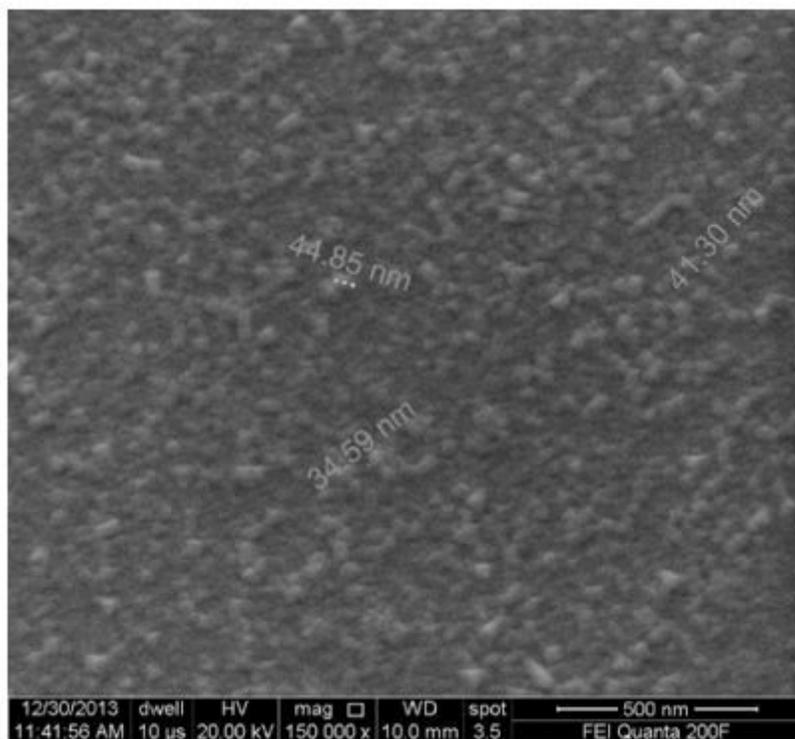


Figure 4

SEM image of 70%PPy + 30%ZnO thin film

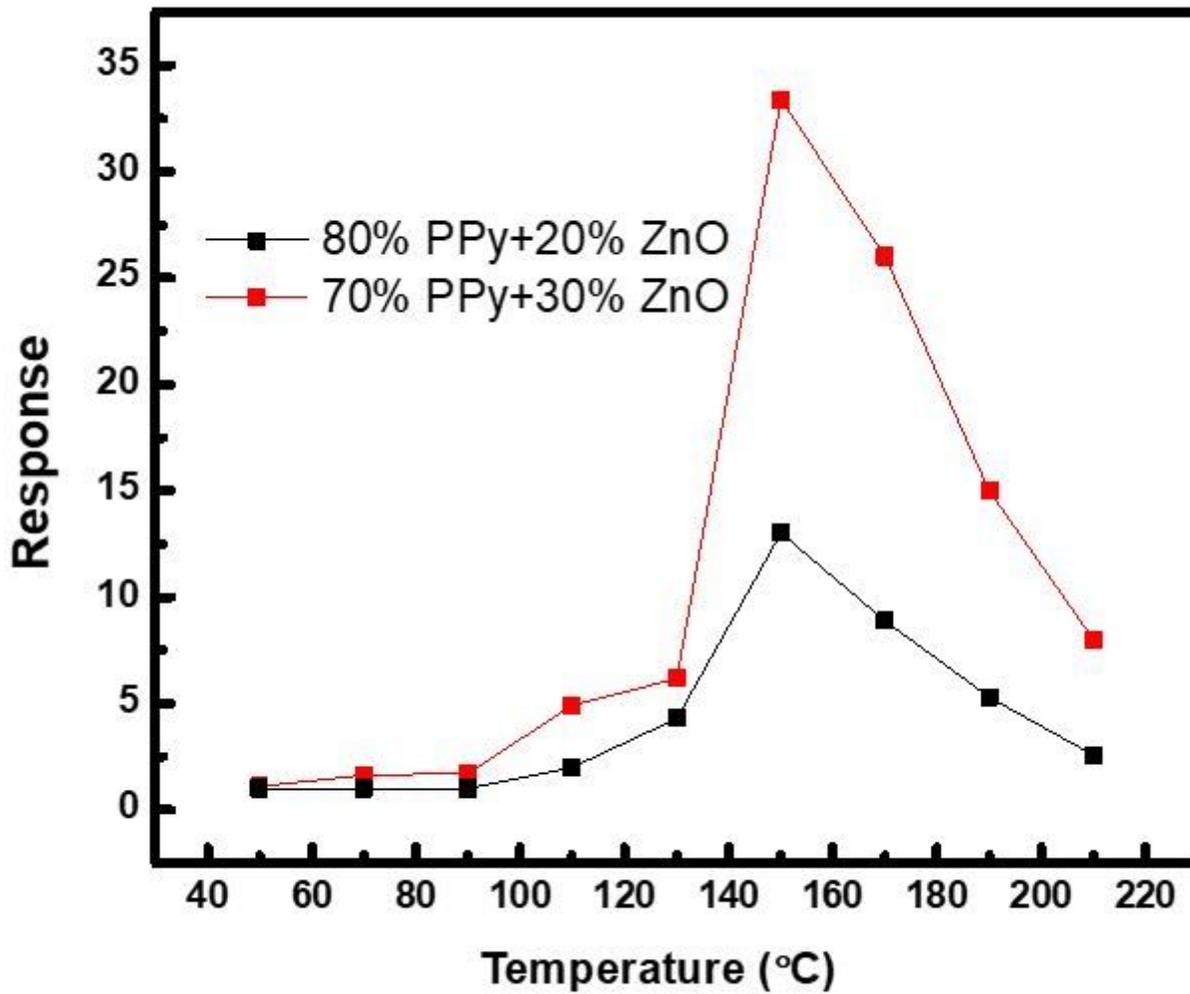
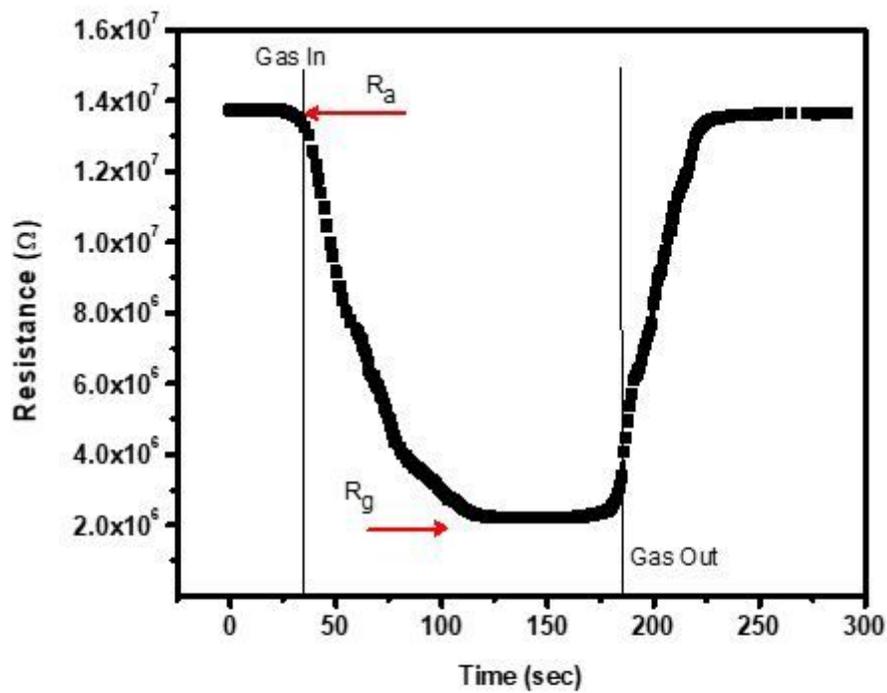
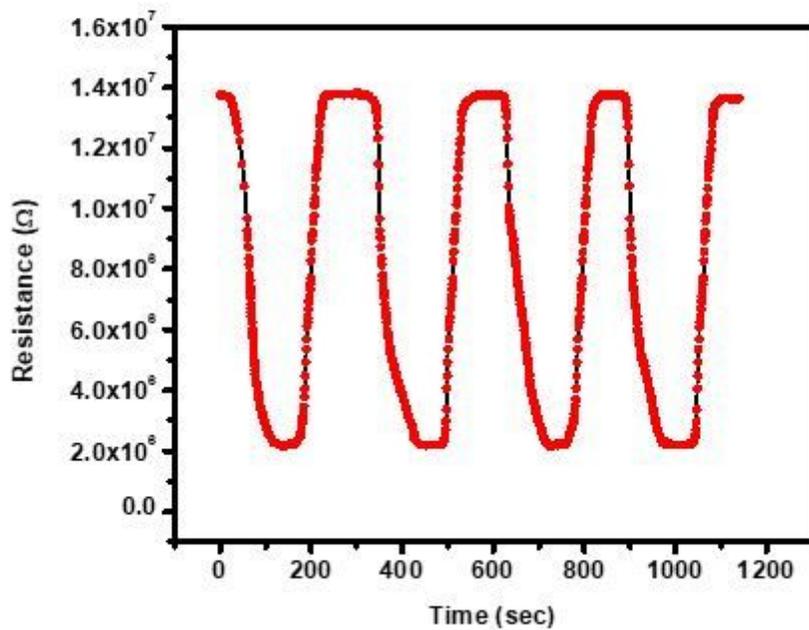


Figure 5

Gas sensing response characteristics of the prepared films towards detecting NH₃ gas



(a)



(b)

Figure 6

(a) Transient Response of the ZnO/PPy sensor at an operating temperature of 130 °C towards 100 ppm of NH₃ gas. (b) Repeatability studies

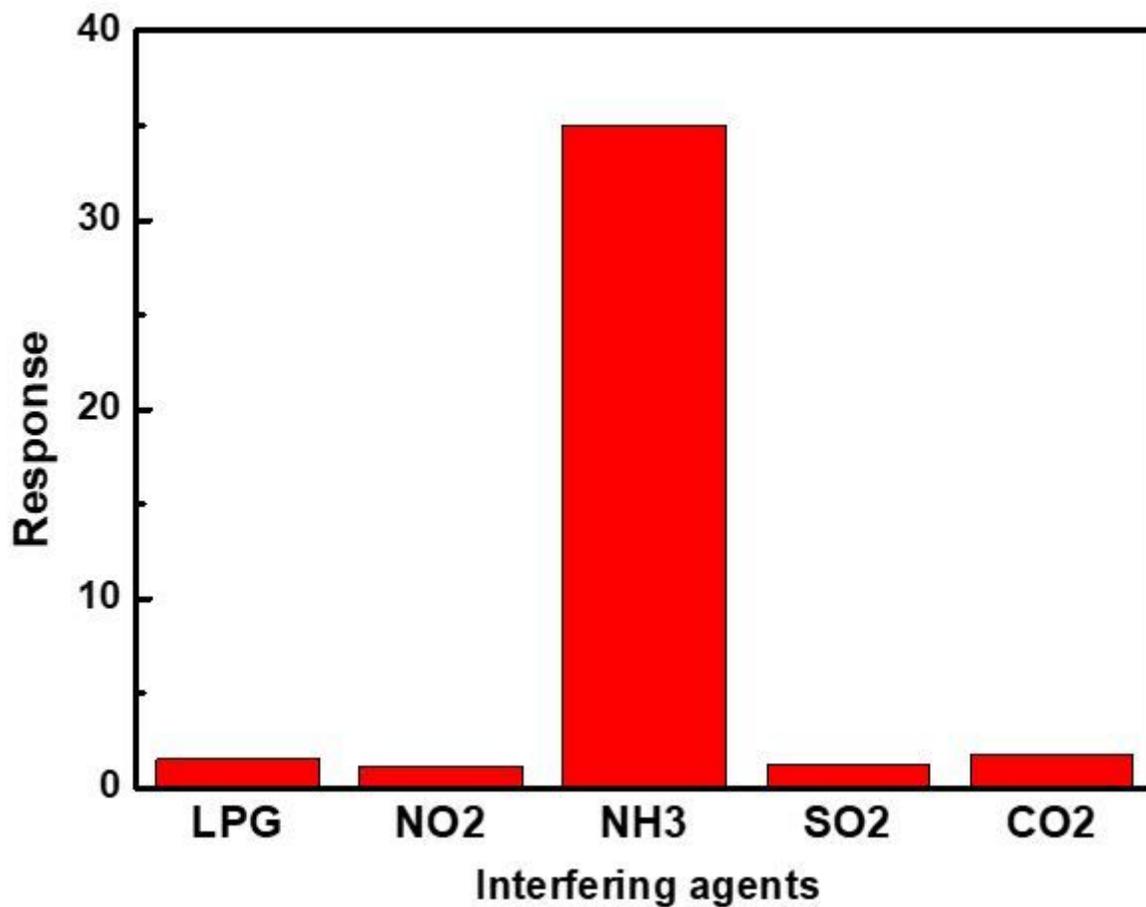


Figure 7

Selectivity graph of the prepared sensor (70%PPy+30%ZnO composite thin film)