Facile Chemical Bath Deposition Method for Interconnected Nanofibrous Polythiophene Thin Films and Their Use for Highly Efficient Room Temperature NO_2 Sensor Application

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Highlights

- Polythiophene thin film gas sensor was prepared successfully by chemical bath deposition technique at room temperature.
- The present study highlights the crucial role of monomer concentration to optimize highly porous interconnected polythiophene network with precise control of pore size.
- Interconnected nanofibrous polythiophene thin film sensor demonstrated its ability to detect very low NO_2 concentration of 1 ppm with precise sensitivity.

Abstract

Interconnected nanofibrous polythiophene (INPTh) film was deposited on the glass substrate through a simple chemical bath deposition method. The influence of monomer concentration on INPTh film properties as well as on NO_2 sensing properties of the film was studied. The morphological and structural studies were carried out using FTIR spectroscopy, FE-SEM microscope, and AFM analysis. The FTIR spectra confirmed the formation of PTH structure. The interconnected nanofibrous surface morphology was observed in FE-SEM images. The roughness of the film and thickness (225 nm to 442 nm) were found to increase with monomer concentration up to 0.5 M, after that, both decreased at 0.6 M monomer concentration. The highest selectivity of PTh thin film towards NO_2 was observed than the other gases like H_2S, SO_2, NH_3, CO and LPG. The influence of film morphology and thickness on gas sensing properties was observed, which was varied with monomer concentration. The film deposited at 0.5 M monomer concentration showed the highest NO_2 gas response of 47.58 % at room temperature. Present

results revealed that monomer concentration was also one of the deposition parameters for tuning the morphological as well as gas sensing properties of the chemical bath deposited PTh film.

Keywords: NO_2 Sensor, Selectivity, Polythiophene, Chemical bath deposition, Polymer thin films.

1. Introduction

Use of organic fuels and other chemicals have become an essential part of the social as well as industrial life. They produce an enormous amount of harmful, toxic, flammable exhaust pollutant gases like NO_x, H_2S, NH_3, Cl_2, etc. in the atmosphere [1,2]. These toxic gases (NO_x (x=1, 2), N_2O_4, etc.) are one of the major exhausted pollutants from the society needs like a vehicle and domestic and industrial exhaust. Direct inhalation of NO_2 can irritate the lungs and lower resistance to respiratory infections. The excess Nitrogen oxide pollution in the air can significantly contribute to the acid rain, photochemical smog (atmospheric reactions that produce ground-level ozone) and eutrophication in coastal waters of the Chesapeake Bay. These processes have adverse effects on both terrestrial and aquatic ecosystems. Due to increase in awareness about the pollution, hygiene, and health care, gas sensors have received considerable attention for their developed. Especially, detection of harmful toxic and flammable exhaust gases at ppm level has become a subject of growing importance for industrial health, safety, and environmental monitoring both at home and workplaces. In last two-three decades, the development of the gas sensor devices has been focused on detection of such toxic and harmful gases. The metal oxide gas sensors based on SnO_2, ZnO, TiO_2, and WO_3, etc. are suffering from the high operating temperature, low sensitivity, and selectivity [3–6], which places the limitations on its practical use in the development of sensor

devices. Therefore, the current research in the field of gas sensor devices has been focused on the development of sensors for the detection of hazardous, toxic and flammable gases, which have the characteristics of high sensitivity, good selectivity, rapid response, and low cost.

Recently, organic conducting polymers (OCP) such as Polyaniline (PANI), Polypyrrole (PPy), and Polythiophene (PTh) are found to be an attractive alternative to the metal oxide gas sensors due to their high sensitivity at room temperature[7–10]. Among these polymers, polythiophene and its derivatives, which have received much attention due to their unique properties like flexibility, good environmental stability, and high electrical conductivity, simple and ease polymerization technique and low cost for the development of various applications. Polythiophene powder and thin films have been prepared by different synthesis techniques, such as chemical oxidative polymerization [9], spin coating [11], vacuum evaporation [12], inkjet printing [13], successive ionic layer adsorption and reaction (SILAR) [14], sol-gel method [15], Langmuir-Blodgett (LB) technique [16], and chemical bath deposition technique [17,18], etc. Polythiophene has also been used for variety of applications like organic light emitting diode [19], gas sensor [9], organic field effect transistor [20], supercapacitor [14], solar cells [21], biosensor [22], microwave shielding [23], photoconductive and photovoltaic devices, and optical modulator devices [24], etc. Furthermore, polythiophene and its derivatives are attractive polymers for sensing application owing to its good environmental and thermal stability, and high electrical conductivity. Polythiophene has identified as one of the sensors materials for different detection of ammonia, trimethylamine, acetone, alcohol and toluene gases at room temperature [10]. Moreover, their surface morphological modification has improved gas sensing properties [25]. Navale et al. [9] report on the 9 % sensing of 10 ppm NO_2 gas for the spin-coated polythiophene

thin films. To our knowledge, there are no reports on the NO_2 gas sensing application by chemical bath deposited polythiophene thin films.

In the present work, we report the deposition of high surface area interconnected nanofibers of polythiophene on glass substrates utilizing simple chemical bath deposition technique. The effect of thiophene monomer concentration on the film thickness and morphology as well as NO_2 sensing properties has been investigated.

2. Experimental

2.1 Materials

The interconnected nanofibers of polythiophene were synthesized using AR grade chemicals, such as Thiophene (99 %, Aldrich Chem. Ltd.), ferric chloride (98 %, Thomas Baker Pvt. Ltd.), methanol (99.5 %, Spectrochem Pvt. Ltd.), and chloroform (99.4 %, Thomas Baker Pvt. Ltd.). The gas sensing measurements were performed on the NO_2, H_2S, NH_3, CO, SO_2, LPG (M/s Shreya Enterprises Pvt. Ltd.) gases.

2.2 Preparation of Polythiophene (PTh) thin film

Interconnected nanofibrous polythiophene thin film was synthesized by chemical bath deposition technique using thiophene as a monomer and ferric chloride as the oxidant, wherein thiophene (AR grade Merck) was purified by distillation before use. Thiophene monomer solution was prepared by dispersing thiophene monomer in chloroform at various concentrations (A-0.3, B-0.4, C-0.5 and D-0.6 M) with continuous stirring for 45 minutes and 0.4 M ferric chloride was dissolved in chloroform to obtain oxidant solution. The deposition bath was prepared with 25 ml oxidant solution, and 25 ml thiophene monomer solution was dropwise added to oxidant solution with continuous stirring. The ultra-cleaned glass substrates of 2.5 cm × 1.2 cm dimensions were immersed vertically in the bath and kept at room temperature. During the initial deposition course,

the glass slides changed its color to brownish, and after two hours finally it became dark brown, which clearly highlights the deposition of INPTh thin films on the glass substrates. The glass substrates coated with INPTh thin films were removed from the bath after 2 h, washed with methanol and chloroform successively for several times to remove unreacted monomer and oxidant from the film, followed by drying in air and preserved in an airtight container. The monomer concentration was varied from 0.3, 0.4, 0.5 and 0.6 M, and the same experiment was repeated to confirm the reproducible formation of INPTh thin films.

2.3 Physicochemical Characterization

The chemical structure and functional groups of INPTh thin films were determined using Fourier Transformed Infrared Spectroscopy (JASCO FT/IR-4100 Series) in the range of 500–4000 cm^{-1} wave number. The surface morphological study was carried out using Field Emission Scanning Electron Microscopy (FESEM, MIRA3 LMH) and Atomic Force Microscopy (AFM, INNOVA 1B3 BE) technique. The thickness of the film was measured using a surface profiler (AMBIOS Technology, USA, XP-1). Elemental analysis was carried out using energy dispersive X-ray analysis (EDAX, Oxford Instrument, INCA-X-ACT). The optical properties of INPTh thin film were studied using UV-Visible spectrophotometer (UV–1800 Shimadzu, Japan). The gas sensing performance was investigated using custom made gas sensing measurement unit (Fig. 1).

2.4 Gas sensing measurements

Fig. 1 shows the schematic experimental setup of the gas sensor measurement unit. The gas response of the film was measured with variation in the resistance of the film in ambient air and the presence of test gas. For the measurement of resistance, two silver electrodes separated by 10 mm, were deposited on INPTh thin film. The resistance was measured using computer controlled Keithley 6514 electrometer system. For monitoring the gas response of the INPTh thin

films for various test gases, the films were mounted in airtight stainless steel container having the volume of 250 cc. The precise concentration of known test gas (NO_2, NH_3, H_2S, SO_2, CO, LPG) was introduced into the chamber by using a syringe. Test gases were commercially acquired from M/s Shreya Enterprises Pvt. Ltd. Mumbai, India. When a steady state was achieved, exposing the sensors to air by opening the lid of the chamber recovery of sensors was recorded. All the gas sensitivity measurements were carried out at room temperature (28 ± 2˚C) with relative humidity (47 ± 2%).

The concentration of injected gas is determined using the formula [9];

$$Conc.of\ test\ gas(ppm) = \frac{Volume\ of\ gas(ml) \times Conc.of\ gas\ in\ chamber(1000ppm)}{Volume\ of\ testing\ chamber\ (250ml)} \quad (1)$$

The response (S) of the sensors was calculated from the response curves using the relation:

$$Response(\%) = \frac{|R_a - R_g|}{R_a} \times 100 \qquad -\ (2)$$

Where, R_a and R_g is the resistance of INPTh thin film sensor in ambient air and the vicinity of the test gas, respectively.

3. Results and Discussion

3.1 Fourier Transform Infrared spectroscopy (FTIR) analysis

The chemical structures of INPTh thin films were probed using FTIR spectroscopy (Fig. 2) in the range of 500 – 4000 cm^{-1} wave number, which has furnished significant information about the nature of chemical bonding and formation of polythiophene. The range of 600-1500 cm^{-1} is the fingerprint region of the polythiophene. The absorption peak at 692 cm^{-1} is attributed for the C-S

stretching in the thiophene ring and the peak at 790 cm^{-1} is due to the C-H out of plane vibration of 2-5-substituted thiophene ring created by the polymerization of thiophene monomer, respectively. The absorption band found at 1029 cm^{-1} is assigned to in-plane stretching vibration of C-H [26]. The absorption band at 1338 $cm^{-1}$and 1456 cm^{-1} arises due to C-C stretching vibrations and C=C symmetric stretching vibrations of thiophene ring, respectively [27–29]. The absorption band at 1732 cm^{-1} has assigned to C=O bond [30] that concludes the inclusion of the small amount of oxygen in a film. The bands between 2872–3063 cm^{-1} are attributed to C-H stretching vibration [31]. Present FTIR result clearly indicates polymerization of the thiophene monomer and no significant change in FTIR spectra was observed at various thiophene monomer concentrations.

3.2 Field Emission Scanning Electron Microscopy (FESEM) and Energy dispersive X- ray Analysis (EDAX)

Fig. 3 shows the surface morphological variations of INPTh thin film prepared by a chemical bath deposition technique. It shows the spongy web like nanofibrous morphology with interconnected nanofibers of average diameter in the range of 35-40 nm forming a porous network. These nanofibers are relatively smooth and homogeneously distributed on the substrate, which provides a high surface to volume ratio. As the concentration of the monomer solution increases the pore size decreases and film become denser. Thus from SEM images, it is observed that the film morphology varies with the monomer concentration.

The EDAX spectra of INPTh thin film shown in Fig. 4 confirm the presence of carbon (C) and sulfur (S) elements in expected stoichiometric form of polythiophene. Other elementals from the substrate are observed in the EDAX spectra. The elemental percentage is shown in Table 1. The concentration of carbon and sulfur has increased with the monomer concentration utilized for synthesis that expected to increase the film thickness. Therefore, we have measured film thickness

by surface profiler technique. The observations made from EDAX are akin to the thickness measurements (Table 2). The thickness of the film has increased from 225 to 442 nm with increase in monomer concentration up to 0.5 M but after that decreased to 303 nm at 0.6 M concentration.

3.4 Atomic force microscopy (AFM)

The three-dimensional analysis of INPTH thin film is performed by AFM as shown in Fig. 5. AFM images confirm that the monomer concentration has strongly affected the growth mechanism of the interconnected nanofibers polythiophene thin films. The obtained images show the surface having a bud like (amalgamated nanofibers) structure. These bud like mountains are vertically oriented, and the number increased with increase in the concentration of monomer, but at the end, at 0.6 M it slightly decreased. The roughness of the film is also evaluated from AFM and shown in Table 2. The roughness of the film has increased with the increase in monomer concentration up to 0.5 M, but after that, it suddenly drops down. The film deposited at 0.5 M monomer concentration has a roughness of ~57.4 nm. These AFM analyses are akin to that of the analysis made from the FESEM images in the Fig. 3.

3.5 Optical properties

The optical studies of polythiophene thin film were carried out by UV–visible absorption spectroscopy and presented in Fig. 6. The spectra show a single wide peak of electronic transition in the thiophene ring at about 522–530 nm which is due to the π-π^* transition. The absorption peak intensity is increased with the monomer concentration up to 0.5 M, after that it suddenly decreased at 0.6 M monomer concentration. The absorption peak intensity is dependent on the thickness of the film given in Table 2.

3.6 Gas sensing properties

3.6.1 Selectivity of INPTh thin film sensor

The gas selectivity is an important parameter of the sensors, which determines whether a sensor can respond selectively to a group of analytes or even specifically to a single analyte. Moreover, the surface roughness affects the sensing properties. Therefore, INPTh film of larger roughness prepared at 0.5 M was used to confirm the selectivity for the H_2S, NH_3, NO_2, CO, SO_2, and LPG gases at a fixed concentration of 100 ppm. A corresponding histogram of responses of INPTh thin films towards these test gases is shown in Fig. 7. The INPTh thin film sensor exhibits the higher response of 47.58% for NO_2 gas than other test gases such as H_2S, NH_3, CO, SO_2, and LPG. From these H_2S, NH_3, CO and LPG are reducing gases. When these gases were exposed to INPTh thin film sensor, the resistance was observed to increase. However the thin film sensor exposed by oxidizing gases like NO_2 and SO_2, the resistance was decreased. The selectivity coefficient (Q) of gas has been calculated by the equation [9],

$$Q = \frac{S_{NO_2}}{S_X} \qquad (3)$$

where S_{NO_2} and S_X are the response of NO_2 gas and interference test gases respectively. The Q values of the INPTh thin films for NO_2 are enlisted in table 3. It is observed that all Q values of the INPTh thin films for NO_2 are higher than 5 which is prime requirement for the good selectivity of INPTh thin film gas sensor [32]. Higher the value of Q_{NO_2} means the sensor has a better ability to discriminate the NO_2 gas amongst the mixture gases.

3.6.2 Effect of INPTh film thickness on NO_2 gas Response of INPTh thin film sensor

Physical-chemical properties of sensor element have a significant effect on its gas sensing performance. Fig. 8 shows the dynamic gas response transients of INPTh thin films deposited with (a) 0.3, (b) 0.4, (c) 0.5 and (d) 0.6 M monomer concentration at fixed NO_2 gas concentration of 100 ppm and room temperature. The NO_2 response increased gradually from 25 to 48 % with

monomer concentration. It achieved the maximum value of 48 % at 0.5 M and reduced to 38 % with a further increase in monomer concentration. The observed behavior can be understood as thiophene monomer concentration increases the INPTh film thickness and morphology varies simultaneously and has a significant effect on NO_2 sensing performance. The observed maximum response of 48% is attributed to the highly porous interconnected polythiophene network like morphology. Such a porous morphology assist NO_2 to react on the INPTh film surface as well as inside porous network more efficiently. However, a highly porous thin film with scattered nanofibers network of the INPTh film deposited at lower (0.3 M and 0.4 M) monomer concentration provided a low effective surface area than that of sample deposited at 0.5 M monomer concentration and resulted in lower NO_2 responses. At 0.6 M monomer concentration (sample d) produced highly dense INPTh thin films of interconnected polythiophene network. The highly dense network obstructed NO_2 gas to react with the surface of INPTh and resulted in the reduced NO_2 response of 38 % than 0.5 M concentration. This evidences the effective role of polythiophene monomer concentration in the alteration of the film thickness and morphology and therefore the NO_2 gas response. The gas response of 47.58 % towards the NO_2 gas at 100 ppm reported here for the nanofibrous morphology of the INPTh thin film is better than the randomly distributed microporous structure of spin coated polythiophene thin film for the NO_2 gas (33 % for 100 ppm gas) [9].

3.6.3 Response of INPTh thin film sensor towards different NO_2 gas concentration

Fig. 9 shows the variation in the response of the INPTh (sample c) sensor at room temperature with the change in the concentration of NO_2. The response of INPTh observed was 3, 14, 20, 27, 35, 48 and 50 % for the NO_2 concentration of 1, 15, 25, 50, 75, 100 and 150 ppm, respectively. The low concentration of gas exposed to the INPTh thin films covers the lower

surface area and results in the lesser interaction between the nanofibers surface and the gas molecules. However, it further increases with the continuous increase of gas exposed and reached its saturation after the gas molecules occupy a maximum surface area of the INPTh nanofibers. Therefore, very small amount of variation in the response (48 to 50 %)has been observed for the NO_2 concentration of 100 and 150 ppm.

3.6.4 Response and recovery times of INPTh thin film sensor

The adsorption mechanism of the gases alters the resistivity of the Polythiophene thin films, the p-type material. [9, 33-36] The The of NO_2 gas extracts electrons from the INPTh thin film after interaction and generates large number of charge carriers i.e. holes in to the film. Therefore, the conductivity INPTh thin film increases and consequently resistance decreases. However, the other gases like H_2S, NH_3, etc. reduces the charge carrier concentration (i.e. holes) of the INPTh thin film by donating electrons and results in the increase in the resistance of the INPTh thin film. The variation in the response of INPTh for these various reducing gasses might have occurred because of their different electron affinity values (NH_3 = 225.4 kJ/mol, H_2S = 55.2 kJ/mol and NO_2 = 289 kJ/mol). The similar behavior has been reported in polythiophene thin films synthesized utilizing spin coating technique [9, 33, 34, 36]. The ability of sensor element to respond quickly to an external stimulus and to regain its original state after input stimulus is cycled up or down are important characteristics defined as response and recovery time, respectively. Characteristically, the response time is defined as the time at which the resistance of the sensor element reaches to 90 % of the saturation value, as a result of exposure to test gas. The recovery time is defined as, the time required for recovering the 90 % of the initial resistance of the sensor element. The rate of adsorption and desorption of test gas, physical properties like thickness, grain size, the microstructure of sensor element have a significant effect on its response and recovery

times. Typical values of response and recovery times are estimated from the dynamic response of INPTh thin films deposited at (a) 0.3, (b) 0.4, (c) 0.5 and (d) 0.6 M thiophene concentration at fixed NO_2 gas concentration 100 ppm (supporting information Fig. S3). The very slight difference in the response time for all the sample deposited at various concentration of thiophene is clearly highlighting the highly adsorptive nature of INPTh thin films towards NO_2 due to their highly porous interconnected network like microstructure. Furthermore, the recovery time has increased from 2152, 3136 and 8050 s for the sample (a), (b) and (c), respectively. This is due to gas reaction species which left behind after the gas interaction results in lowering desorption rate, and hence the recovery time increased with increase in the porosity of INPTh thin films.

3.6.5 Reproducibility and stability of INPTh thin film sensor

The reproducibility and long-term stability are crucial parameters for evaluating the performance of a sensor. Reproducibility of INPTh thin film sensor is evaluated by measuring the gas response for four consecutive exposures of 25 ppm of NO_2. During the test, no significant variation has observed as shown in Fig. 10. The obtained results clearly underscored the good reproducibility upon repeated exposure and removal of 25 ppm NO_2 gas. Long-term stability of INPTh thin film sensor has evaluated by measuring the continuous NO_2 gas responses with 10 days intervals between the each measurement. The tests are performed for several times as shown in Fig. 11. INPTh thin film sensor exhibited the maximum response of 48 % for the opening day and dropped down to 34 % after 50 days. However, after 50 days a relatively stable gas response performance of INPTh thin film sensor was observed for succeeding days with a slight variation.

4 Conclusions

Polythiophene thin films with an interconnected network like morphology and different thicknesses have been deposited by chemical bath deposition method on glass substrate. Effect of

thiophene monomer concentration on polythiophene thin films is studied to optimize the properties of INPTh thin films. The present study clearly highlighted the crucial role of monomer concentration to optimize highly porous interconnected polythiophene network with precise control of pore size. The present INPTh thin films successfully demonstrated for the gas sensing properties. INPTh thin film sensor studied for the various test gases such as NH_3, H_2S, SO_2, CO, LPG and NO_2 at room temperature. Among these interfering gases INPTh thin film sensor demonstrated a high response, and selectivity, towards NO_2 gas. The selectivity study showed that INPTh thin film sensor is most selective to NO_2 against other interfering gases. Therefore NO_2 sensing properties of INPTh thin films are studied in detail. INPTh thin film sensor demonstrated its ability to detect very low NO_2 concentration of 1 ppm with the response of 2.46%.

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Figure Captions:

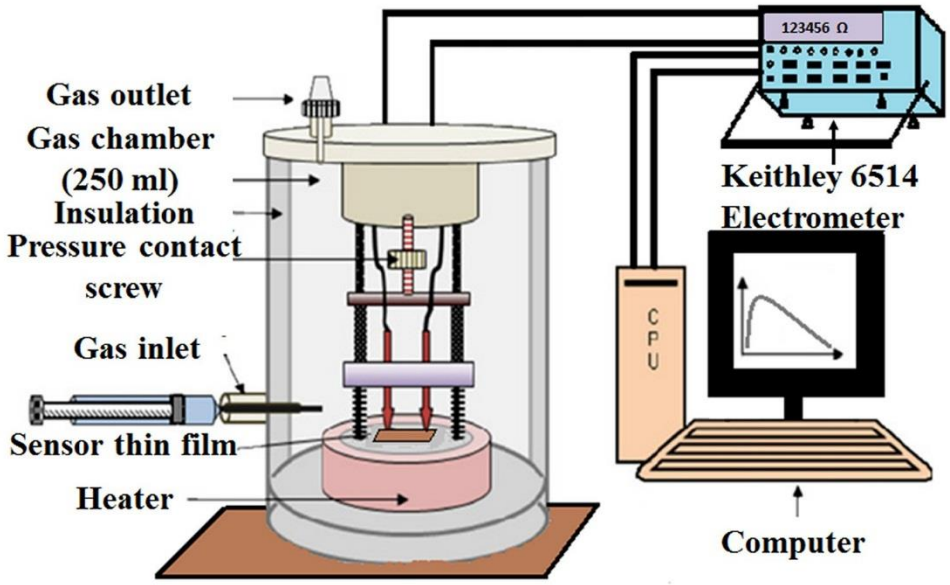

Fig. 1. Schematic of the experimental setup for gas sensing measurement.

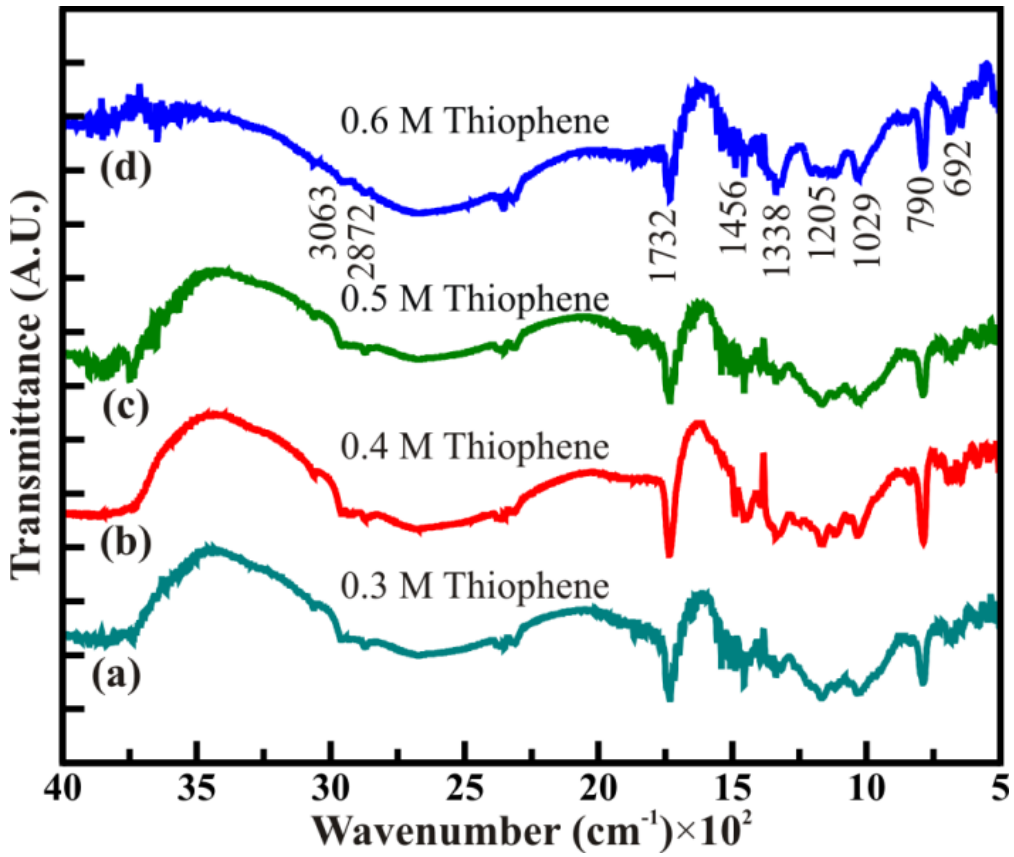

Fig. 2. FTIR of INPTh thin films deposited at (a) 0.3, (b) 0.4, (c) 0.5 and (d) 0.6 M thiophene concentration.

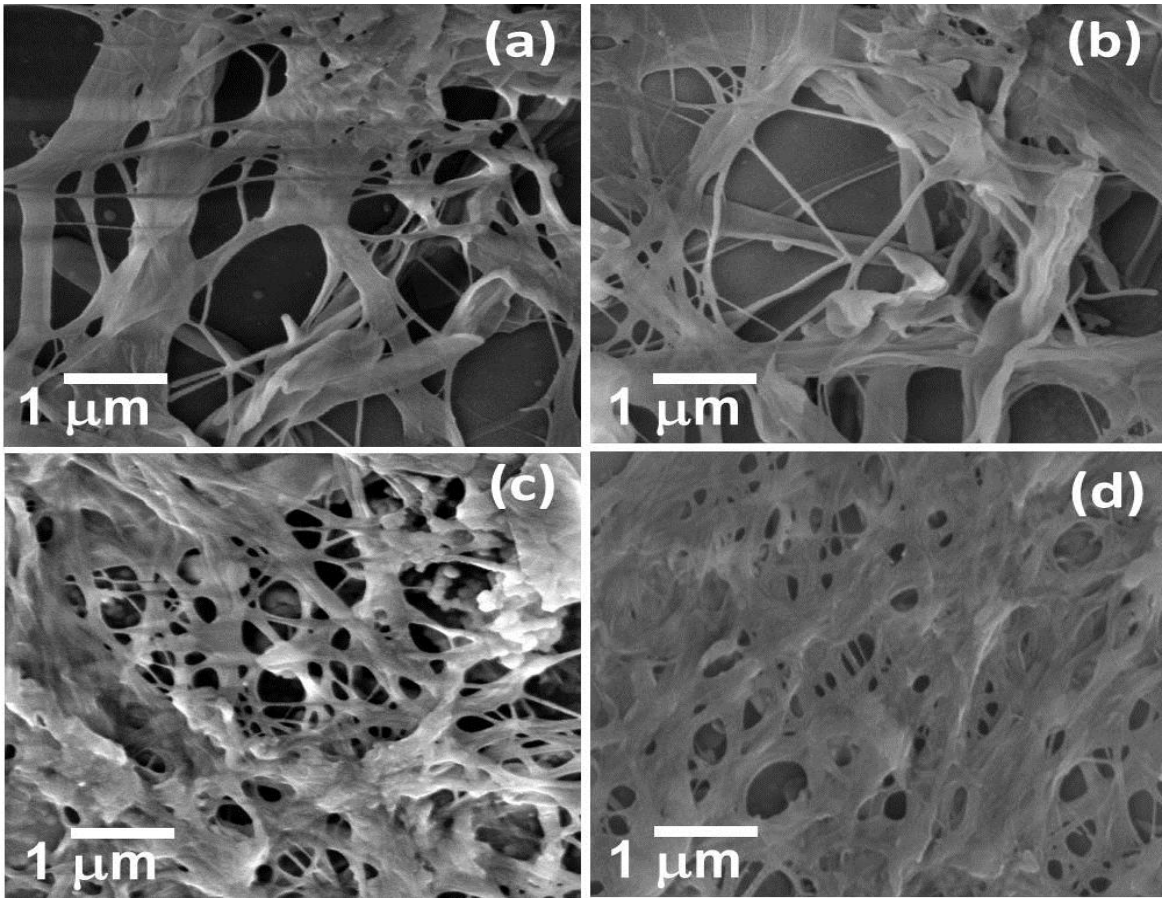

Fig. 3. FESEM micrograph of INPTh thin films deposited at (a) 0.3, (b) 0.4, (c) 0.5 and (d) 0.6 M thiophene concentration.

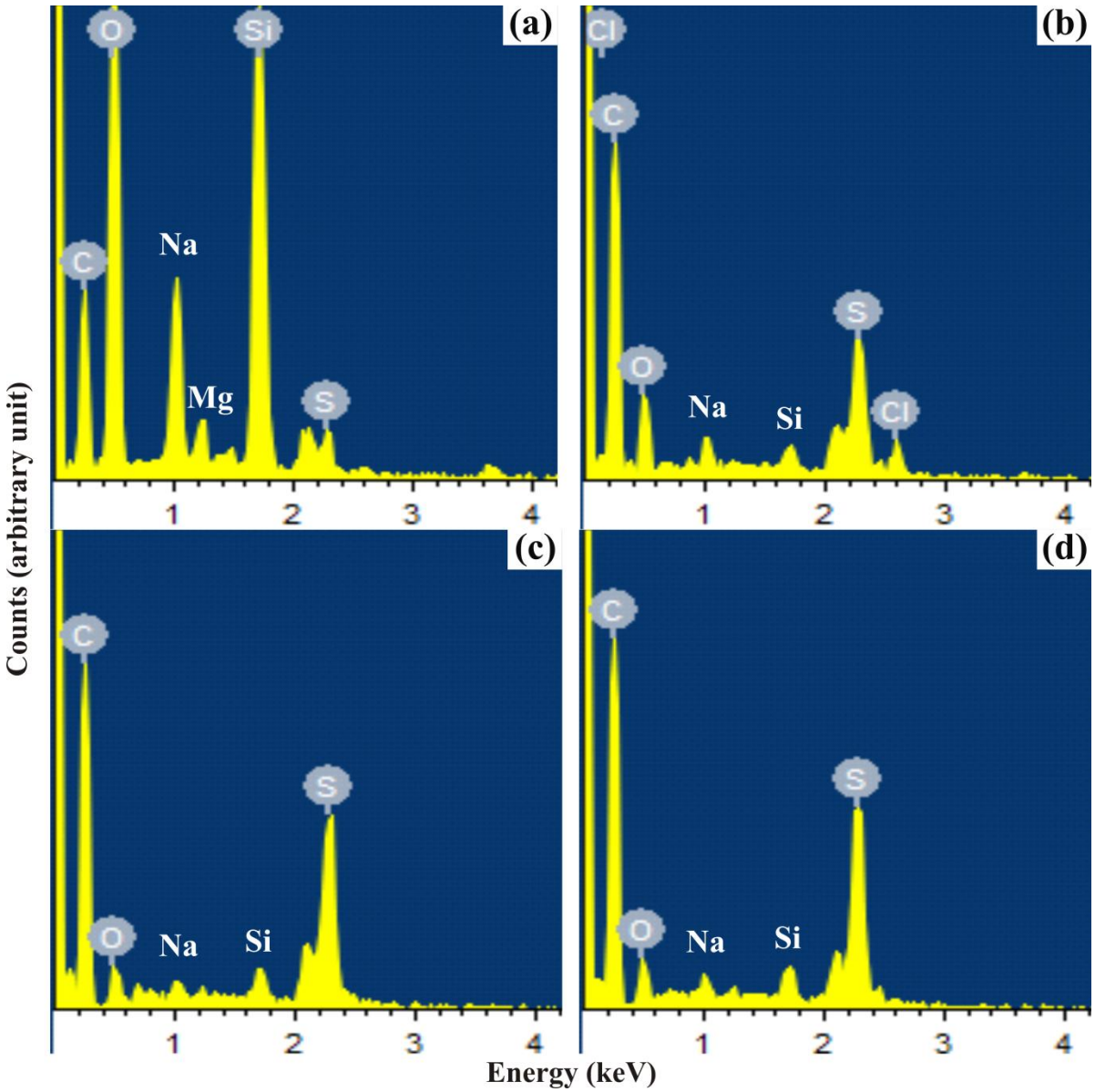

Fig. 4. EDAX spectrum of INPTh thin films deposited at (a) 0.3, (b) 0.4, (c) 0.5 and (d) 0.6 M thiophene concentration.

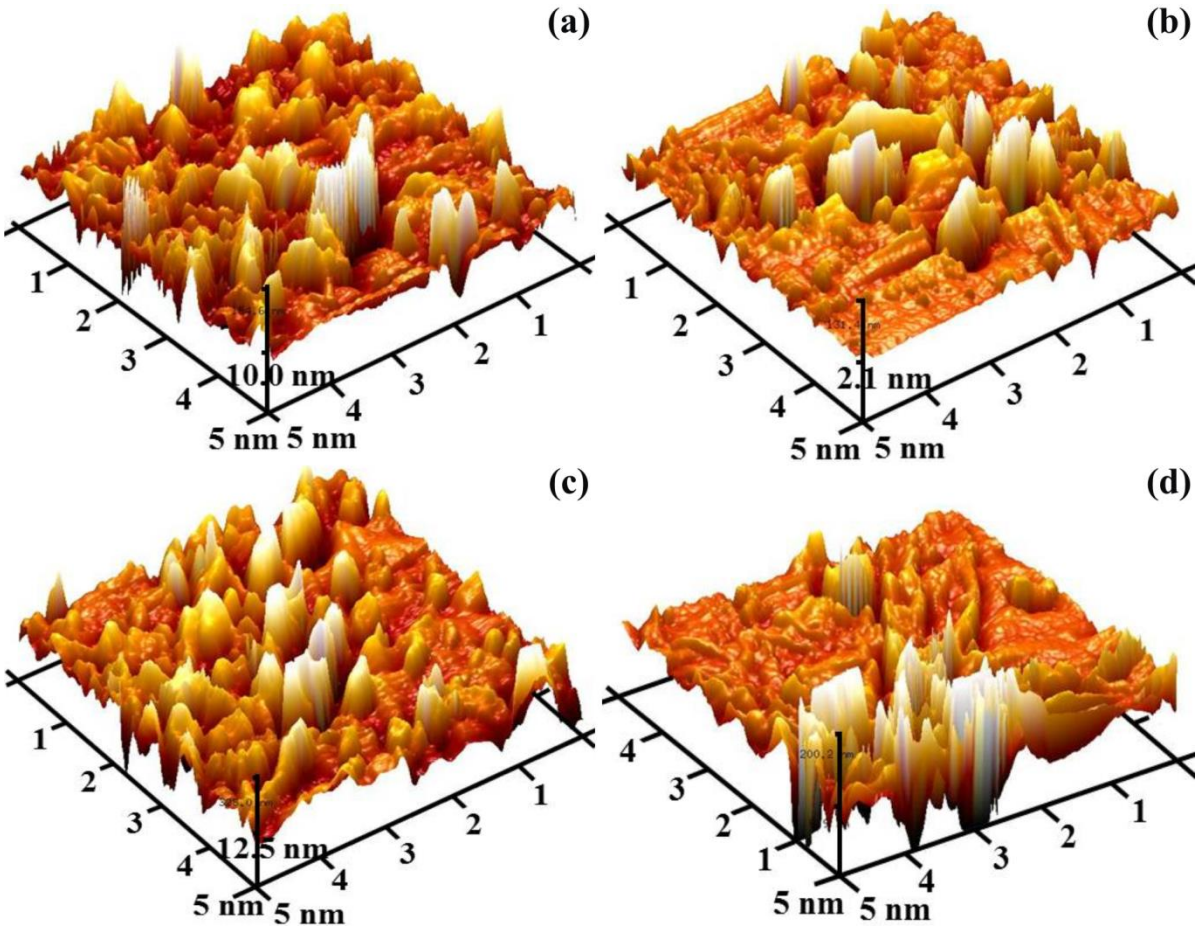

Fig. 5. 3-D AFM images of INPTh thin films deposited at (a) 0.3, (b) 0.4, (c) 0.5 and (d) 0.6 M thiophene concentration.

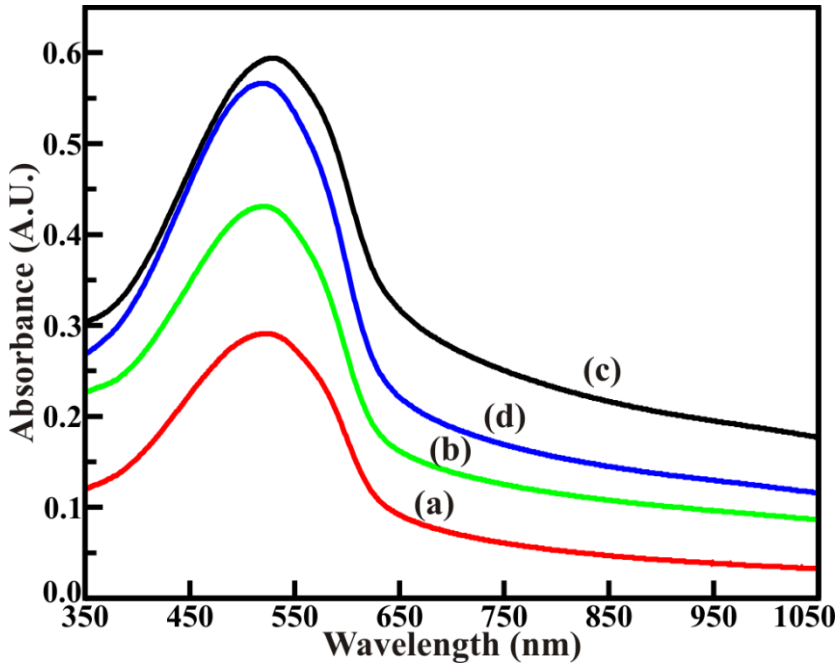

Fig. 6. UV-Vis spectra of INPTh thin films deposited at (a) 0.3, (b) 0.4, (c) 0.5 and (d) 0.6 M thiophene concentration.

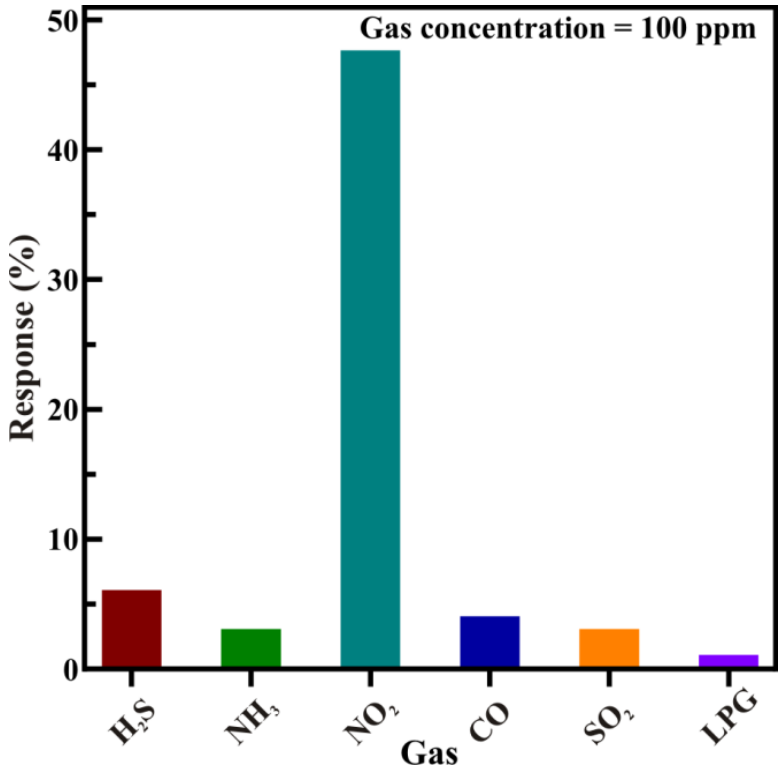

Fig. 7. Histogram representing selectivity of INPTh thin films (film thickness 442.8 nm) sensor for 100 ppm of various gases operating at room temperature.

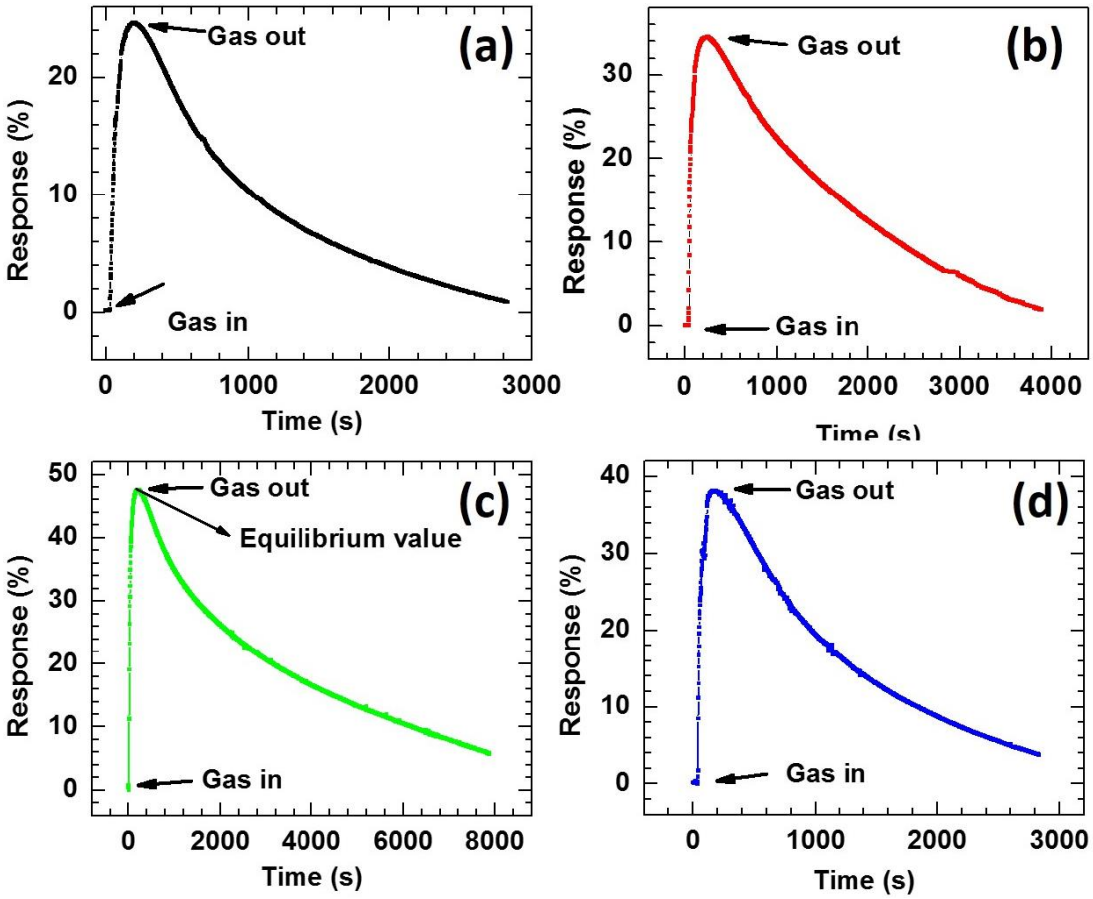

Fig. 8. Response of INPTh thin films deposited at (a) 0.3, (b) 0.4, (c) 0.5 and (d) 0.6 M thiophene concentration at fixed NO_2 gas concentration 100 ppm.

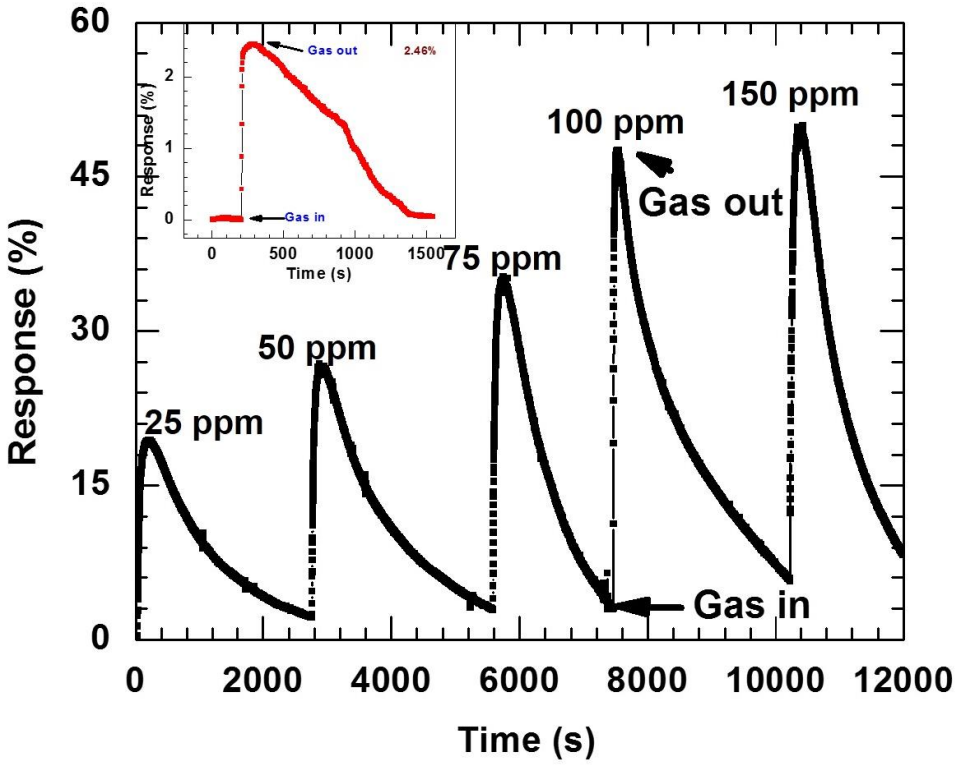

Fig. 9. Dynamic response of INPTh thin film sensor (film thickness 442.8 nm) towards various concentrations of NO_2 gas.

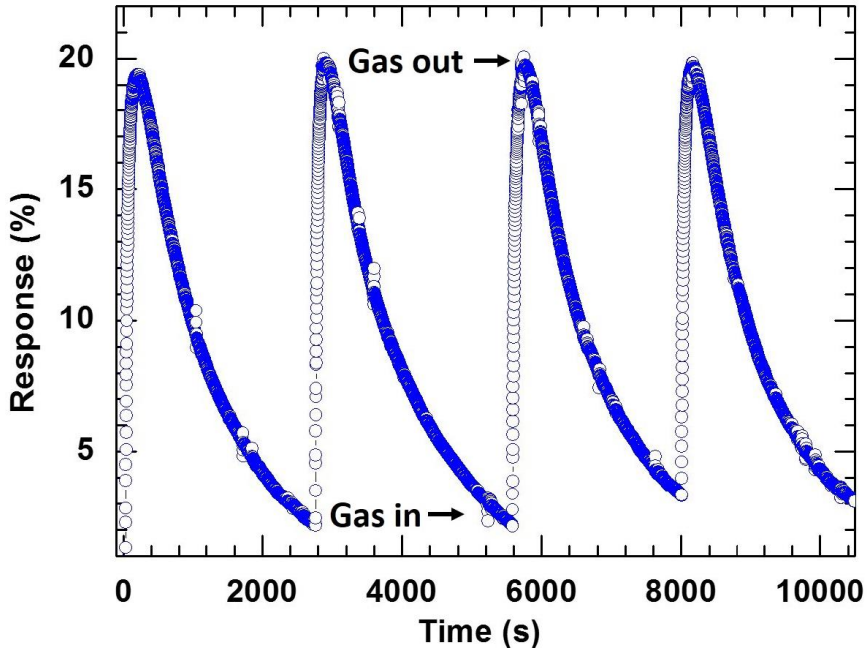

Fig.10. Reproducibility study of INPTh thin film (film thickness 442.8 nm) for 25 ppm NO_2 gas.

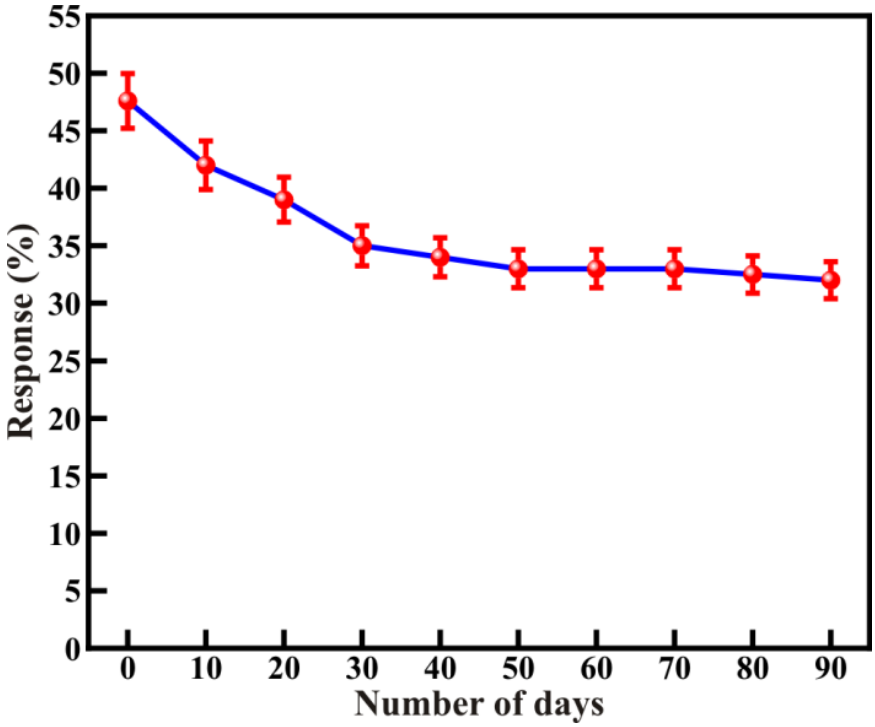

Fig.11. Stability study of INPTh thin film sensor for NO_2 gas at room temperature for fixed concentration 100 ppm.

Table captions:

Table 1 Atomic percentage of interconnected nanofibrous polythiophene thin films (a) 0.3 M, (b) 0.4 M, (c) 0.5 M and (d) 0.6 M by EDAX.

Sample code / Elements	Atomic weight %			
	(a)	**(b)**	**(c)**	**(d)**
C K	28.86	76.27	77.27	79.03
S K	1.71	9.26	17.02	14.64
O K	47.46	11.54	5.70	6.32
Si K	19.18	-	-	-
Na K	4.79	-	-	-
Cl K	-	2.93	-	-

Table 2 Thickness and roughness of interconnected nanofibrous polythiophene thin films (a) 0.3 M, (b) 0.4 M, (c) 0.5 M and (d) 0.6 M.

Sample	Thickness(nm)	Roughness(nm)
(a)	225.1	18.3
(b)	291.4	27.5
(c)	442.8	57.4
(d)	303.7	24.5

Table 3 Q- Values of the sensor made by the interconnected nanofibrous polythiophene thin films for the NO_2 as target gas.

Gases	Q values
H_2S	6.93
NH_3	13.86
CO	10.395
SO_2	13.86
LPG	47.58