# STUDY ON SENSING PROPERTIES OF NANO $SnO_2$ –$TiO_2$ COMPOSITES WITH EFFECT OF PPY POROUS LAYER FOR SENSING $NH_3$ GAS

**K.B. Raulkar[*], K.M. Mude[1], B.M. Mude[2], V.M. Mayekar[2], S.M. Yenorkar[3], R.R. Mistry[4], R.N. Zade[5], S.M. Warbhe[6], P.S. Nandurkar[7], A.N. Patange[8]**

[*]Department of Physics, Vidya Bharati Mahavidyalaya, Amravati, MS, India.
[1]Department of Physics, Bhavan's College, Andheri (W), Mumbai, MS, India.
[2]Ramnarain Ruia College, Matunga (E), Mumbai, MS, India
[3]Department of Physics, Shri Shivaji College, Parbhani, MS,India.
[4]Department of Physics, Deogiri College, Aurangabad, MS,India.
[5]Department of Chemistry, Siddharth College, Fort, Mumbai, MS, India.
[6]Department of Mathematics, SGBAU, Amravati University, Amravati, MS, India.
[7]Department of Chemistry, SGBAU, Amravati University, Amravati, MS, India.
[8]Department of Chemistry, Bhavan's College, Andheri (W), Mumbai , MS, India.
* Corresponding Author email. kbraulkar2016@gmail.com

## ABSTRACT

*Ammonia gas detection is an important issue for a lot of applications: leak detection in industry, agriculture, cooling systems, and medical diagnosis (breath biomarker for non-invasive diagnostic of renal disease). For this, sensor had been prepared with the thick film on cleaned glass platewith $Al_2O_3$ as highly porous substrate. $SnO_2/TiO_2$ composite layers were grown on the substrate with the help of screen printing technique to form uniform layers. PPy layer was deposited on this $SnO_2/TiO_2$ composite layer. The sensor was tested for with and without PPy layer to sense $NH_3$ gas. Five sensors S1, S2, S3, S4 and S5 were fabricated for different $SnO_2/TiO_2$ composites. It was found that $S_5$ sensor was best among the prepared sensors to sense ammonia gas at room temperature. The maximum reported value of sensitivity of S5 sensor is 0.93 at 140 mm and remains constant for higher ammonia concentration (upto 200 ppm).*

***Keywords:*** *$SnO_2$-$TiO_2$ composites thick layer, PPy, $Al_2O_3$, Screen Printing Technique, sensitivity*

## 1. Introduction

In today's world, nanostructure metal oxides have attracted a lot of applications in sensors due to their technological attentions and outstanding properties. Nanomaterials properties such asmagnetic, optical, catalytic and electronic depend strongly on size, structure and shape of nanoparticles. Another reason for attraction of scientists' attention towards nano size particles is that they behave differently from bulk materials. Decreasing particle size,led to change the band structure of the semiconductors.

High conductivities exhibited by $SnO_2$as it is an abundant, low cost, natively n-type andas it is wide band gap oxide.$SnO_2$ becomes the best and popular functional material because of good electrical and optical properties as well as large band gap energy [1-5]. $SnO_2$ based composite coaxial nanocables with multiwalled carbon nanotube and PPy via a simple one pot chemical route was successfully synthesized by Shao *et al.* [6]

Ammonia is most important compound for detection as it is volatile in human breath and it's a biomarker for asthma andrenal diseaseearly detection. About 0.17 to 1.8 ppm ammonia is exhaled by a normal healthy person while patients with extreme renal disorders or ulcers exhale above 0.8 ppm to 14 ppm [7-8].$NH_3$ sensors based on conducting polymers have shown better sensing responses among various sensors based on different materials [9-10]. Conducting polymer-based sensors can work at room temperature unlike the metal-oxide-based sensors which require high operating temperature to activate the absorption and desorption of $NH_3$ for its detection. Low operating temperature leads to an increase in sensor life time and a decrease in power consumption. It also makes sensor operation prominent [11, 12]. Conducting polymers have excellent notable features, such as low energy optical transitions,controllable electrical conductivity, low ionization potential, and high electron affinity, due to which they are suitable candidates for sensing applications [13, 14].

In the present work, the sensors S1, S2, S3, S4 and S5were fabricated for different $SnO_2/TiO_2$ composites by using screen printing technique [15-17]. The prepared sensors are exposed to

$NH_3$ gas to check the response at lower concentration of ammonia at room temperature (300 K). The porosity of the materials was checked by SEM and response and recovery times were determined.

## 2. Experimental

### 2.1. Synthesis of $SnO_2$ Nanoparticles

GR grade chemicals of Sd-fine, India had been used for the study having purity 99.99%. $SnO_2$ had been prepared by taking 2g (0.1 M) of stannous chloride dehydrate ($SnCl_2.2H_2O$) which was dissolved in 100 ml $H_2O$. With magnetic stirring, after complete dissolution, 4 ml ammonia solution was added to thisaqueous solution. Solution was stirred for about 30 minutes to get white gel precipitate.

Precipitate was leftto settle for 9 to 10h. The thick precipitate was then filtered and cleaned with distilledwater 3-4 times by using de-ionizedwater. The washedand cleaned precipitate wascombined with 0.27g carbon black powder (charcoal activated). The mixer was kept in vacuum oven at 85ºC for about 1 day to obtain the mixer in powder form. The dried sample then grinded to obtain fine power.Thisfine product of nanopowder of $SnO_2$wascalcinated at 700°C upto7 h in the auto-controlledmuffle furnace (Gayatri Scientific, Mumbai, India.) to eliminate the impurities from product completely.

### 2.2. Synthesis of $TiO_2$ Nanoparticles

In the synthesis of $TiO_2$ particles,Titanium tetra iso-propoxide was used as a precursor and was mixed withHCl,ethanol and deionized water mixture. It was then stirred for half an hour, in pH range of 1.5. 10ml of deionized water was added to the above mixture and further stirred for 2 hours at room temperature. Finally the solution was dried at temperature and the powder was heated at 120ºC for 1 hour to get $TiO_2$ nanoparticles [18].

### 2.3. Synthesis of Polypyrole (PPy)

The Py monomer, anhydrous iron (III) chloride ($FeCl_3$) and methanol were used for synthesis of PPy [19]. The solution of 7 ml methanol and1.892 g $FeCl_3$ was first prepared in round bottom flask. Then 8.4 ml Py monomer was added to ($FeCl_3$+methanol) solution with constant stirring in dark. The amount of Py monomer added to the solution (1/2.33 times of $FeCl_3$) was in such a way to get maximum yield. The resulting black precipitates were filtered and washed with copious amount of distilled water until the washings are clear. PPy so obtained was dried by keeping in oven at 600°C for 3 h.

### 2.4. Preparations of thick films

Thick films of sensors were fabricated by screen printing technique. The thixotropic pastewas formulated by mixing the sintered fine powder of pure and composite nano-powder of $SnO_2$and $TiO_2$ in different weight percentage with a solution of ethyl cellulose (as 10% temporary binder) in a mixture of organic solvent such as butyl cellulose, butyl carbitol acetate and turpineol. In the formulation of the chemical paste, the ratio 75:25 of inorganic to organic parts was maintained. The paste was then used to prepare thick films of pure and composite materials of $SnO_2$ and$TiO_2$and it was screen printed out on a cleaned glass substrate having $Al_2O_3$ as base, as show in figures 1 and 2 respectively.

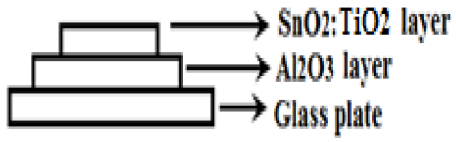



**Figure 1.Sensor without PPy layer**

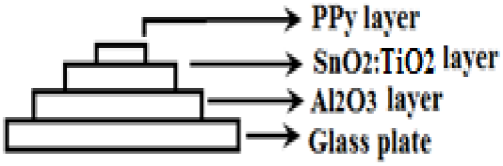



**Figure 2.Sensor with PPy layer**

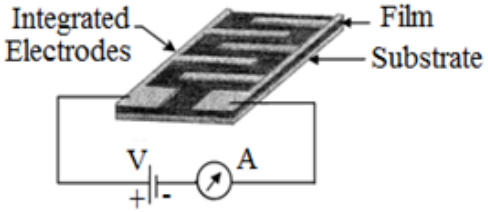



**Figure 3.Voltage drop method**

For an hour, the prepared films were dried at 80-100°C in calibrated oven. Due to this all theorganic materials (in the form of binders) and organic impurities were evaporated. The surface resistance measurements were done by forming electrodes of silver paint on adjacent

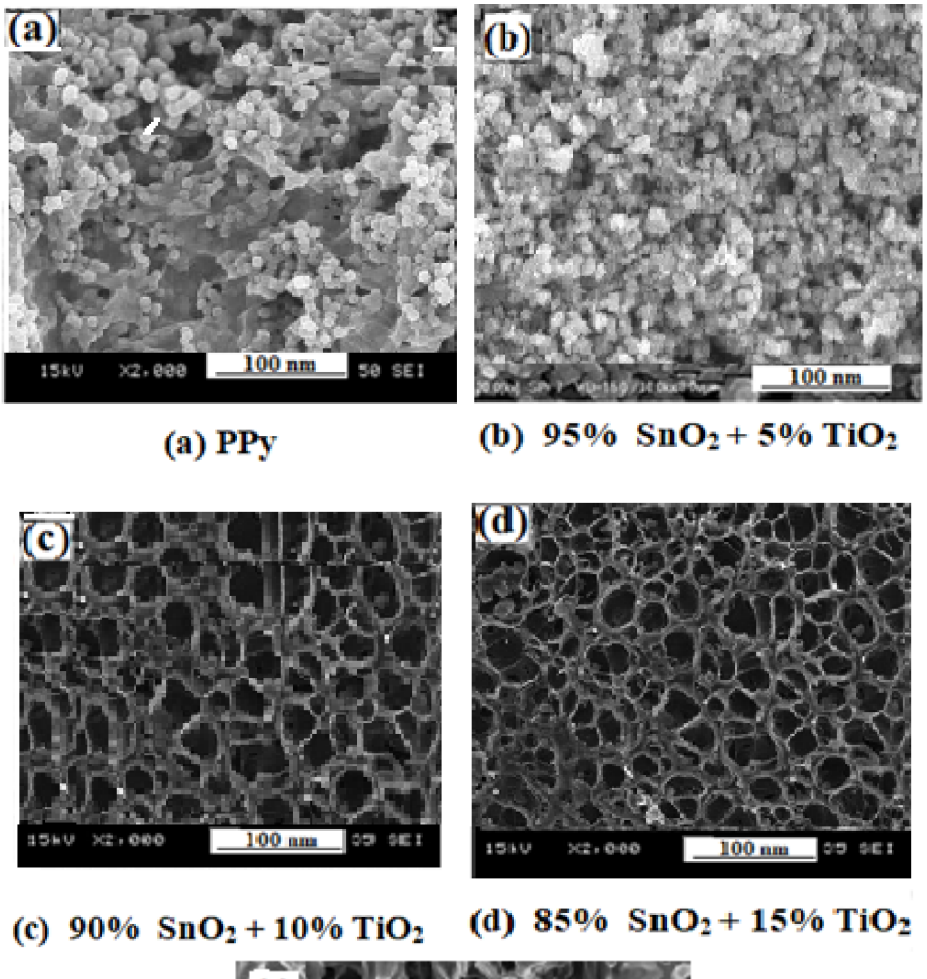
sides of the films. For drying the silver paint, the films were further heated at about 80°C for half an hour. The prepared sensors are listed below in table 1.

**Table 1: The prepared sensors composition and sample code**

| Sr. No. | Nano-Composites | Sample codes |
|---|---|---|
| 1. | 95% $SnO_2$ + 5% $TiO_2$ | S1 |
| 2. | 90% $SnO_2$ + 10% $TiO_2$ | S2 |
| 3. | 85% $SnO_2$ + 15% $TiO_2$ | S3 |
| 4. | 80% $SnO_2$ + 20% $TiO_2$ | S4 |
| 5. | Best sensor + ppy layer | S5 |

## 3. Results and Discussions

### 3.1. SEM (Scanning Electron Microscope) study




(a) PPy

(b) 95% $SnO_2$ + 5% $TiO_2$

(c) 90% $SnO_2$ + 10% $TiO_2$

(d) 85% $SnO_2$ + 15% $TiO_2$

(e) 80% $SnO_2$ + 20% $TiO_2$

**Figure 4: SEM of materials**

SEM photos exhibited that, per inch from each region, number of pores is different. Hence, average number of pores was taken for comparative study. From each SEM picture, porosity was calculated by taking one inch region in consideration and it was manifested that sponginess (porosity) of 85% $SnO_2$ + 15% $TiO_2$ is more than among the prepared materials. SEM, also exhibited more porosity of PPy. Because of high porosity, the ammonia gas will be absorbed more and hence it will be sensed more i.e. sensitivity increases due to more porosity. Some of the pores are cylindrical and some are spherical, some are elongated and some pores have elliptical shapes. All these pores formed cavity which helped in the absorption of the gas.

**Sensitivity:**

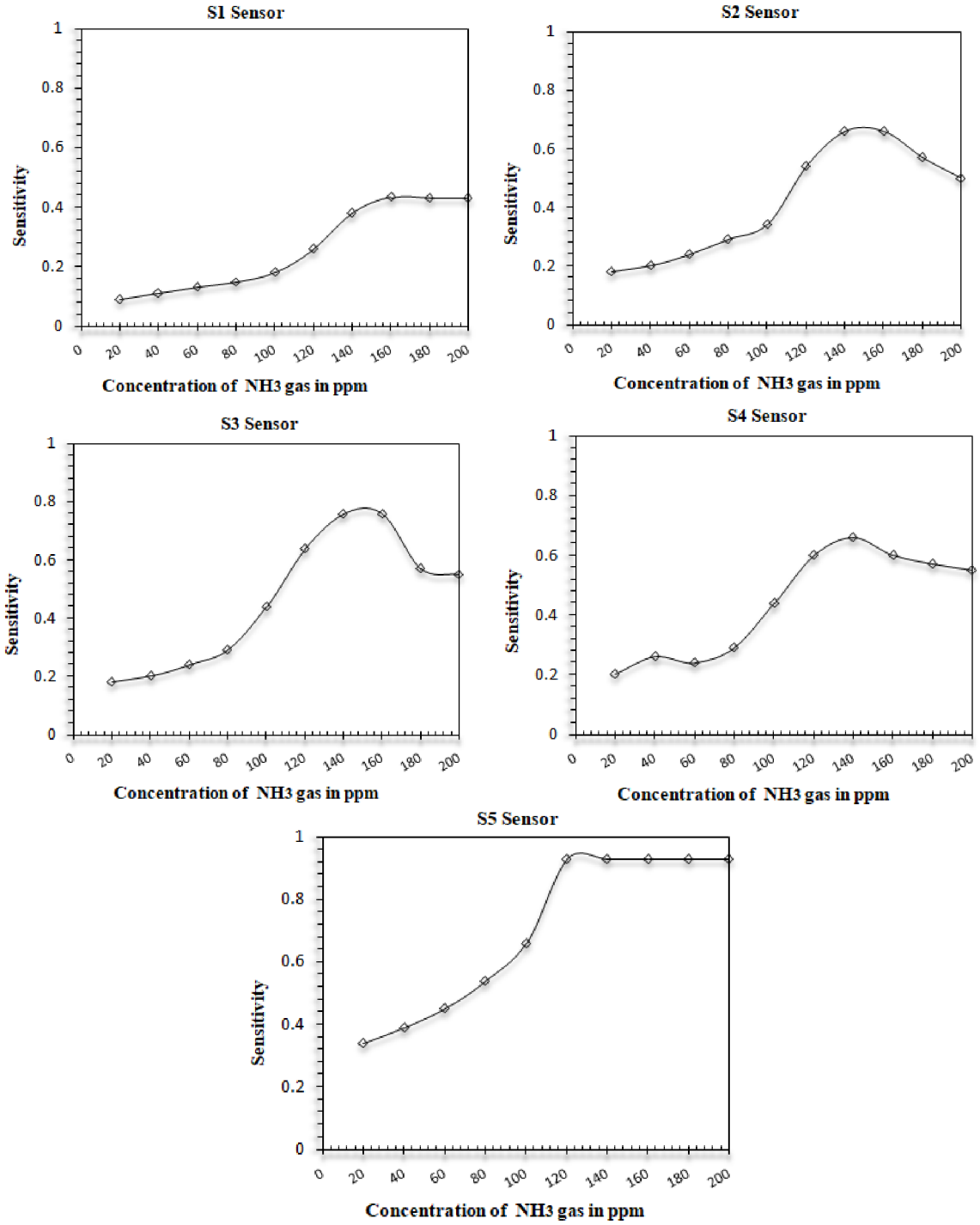



**Figure 5. Variation of sensitivity of S1, S2, S3, S4 and S5 sensors with $_{NH32}$ gas concentration (ppm) at room temperature (303 K).**

Sensitivity is defined as the ratio of change in resistance of the sensor due to presence of gas to the resistance in air environment and is given by

$$S = \frac{\text{Change in resistance}}{\text{Original resistance}} = \frac{R_{gas} - R_{air}}{R_{air}}$$

Where,

$R_{gas}$ = Resistance of the sensor in presence of $NH_3$ gas environment and

$R_{air}$ = Resistance of the sensor in presence of air.

From figure 5, for sensor S1, it is manifested that upto 100 ppm of ammonia gas concentration,sensitivity is low and beyond that sensitivity slowly increases and becomes constant. For sensor S2, with increase in ammonia gas concentration, sensitivity increases and becomes maximum at about 140 ppm gas concentration and with further increase in concentration, sensitivity decreases. Its maximum reported value is 0.66. S3 sensor showed more sensitivity among the sensors at about 150 ppm and then sensitivity decreases with further increase in gasconcentration. In case of S4 sensor, at 40 ppm sensitivity increases and with further rise in ppm of $NH_3$ gas, sensitivity increases and becomes maximum at 140 ppm and then decreases. Its maximum noted value is 0.61. S5 sensor is the modified S3 sensor. S5 sensor is constructed by forming PPy layer over the(85% $SnO_2$ + 15% $TiO_2$) layer. Since it was taken into consideration that, S3 sensor showed more response and PPy has more porosity, so both layers would show enhanced response and hence S5 sensor was fabricated. In case of sensor S5, it was manifested that as ammonia gas concentration increases, sensitivity increases till 110 ppm and from 120 ppm sensitivity becomes maximum and remains constant. The maximum reported value was0.93.

## 4. Conclusion

SEM pictures exhibited more porosity for PPy and (85% $SnO_2$ + 15% $TiO_2$) and hence more gas absorptivity. Threshold value of sensitivity of the S3 sensor was found to be 0.76 at 140 ppm ammonia gas concentration and at 300 K (room temperature). This more response is due to the more porosity of (85% $SnO_2$ + 15% $TiO_2$) among the prepared samples. In S5 sensor, as PPy has more porosity and S3 sensor already showed more porosity. Therefore in S5 sensor, S3 sensor acted as porous base and PPy acted as active layer. When ammonia gas molecules interacted with PPy molecules, they lose their energy and will be absorbed by PPy molecular whirlpool. Also S3 sensor base supported it and hence sensitivity increases more.

## 5. Acknowledgement

The authors would like to acknowledge Department of Physics, Vidya Bharati Mahavidyalaya, Amravati (India) for providing Research center to carry on this work.

## References

1. Ly, A., Luo, Y., Cavaillès, G., Olivier, M. G., Debliquy, M., & Lahem, D. (2020). Ammonia sensor based on vapor phase polymerized polypyrrole. Chemosensors, 8(2), 38.
2. Tai, H., Wang, S., Duan, Z., & Jiang, Y. (2020). Evolution of breath analysis based on humidity and gas sensors: Potential and challenges. Sensors and Actuators B: Chemical, 318, 128104.
3. Nakhleh, M.K., Amal, H., Jeries, R., Broza, Y.Y., Aboud, M., Gharra, A., & Haick, H. (2017). Diagnosis and classification of 17 diseases from 1404 subjects via pattern analysis of exhaled molecules. ACS nano, 11(1), 112-125.
4. Sachan, A., Castro, M., Choudhary, V., & Feller, J. F. (2018). Influence of water molecules on the detection of volatile organic compounds (VOC) cancer biomarkers by nanocomposite quantum resistive vapor sensors vQRS. Chemosensors, 6(4), 64.
5. Li, W., Liu, H., Xie, D., He, Z., & Pi, X. (2017). Lung cancer screening based on type-different sensor arrays. Scientific reports, 7(1), 1-12.
6. Shao, Q. G., Chen, W. M., Wang, Z. H., Qie, L., Yuan, L. X., Zhang, W. X., &

Huang, Y. H. (2011). SnO2-based composite coaxial nanocables with multi-walled carbon nanotube and polypyrrole as anode materials for lithium-ion batteries. Electrochemistry communications, 13(12), 1431-1434.

7. Tang, X., Raskin, J.P., Kryvutsa, N., Hermans, S., Slobodian, O., Nazarov, A.N., & Debliquy, M. (2020). An ammonia sensor composed of polypyrrole synthesized on reduced graphene oxide by electropolymerization. Sensors and Actuators B: Chemical, 305, 127423.
8. Güntner, A.T., Righettoni, M., & Pratsinis, S. E. (2016). Selective sensing of NH3 by Si-doped α-MoO3 for breath analysis. Sensors and Actuators B: Chemical, 223, 266-273.
9. Dai, M.Z., Lin, Y.L., Lin, H.C., Zan, H.W., Chang, K.T., Meng, H.F., & Cheng, H. (2013). Highly sensitive ammonia sensor with organic vertical nanojunctions for noninvasive detection of hepatic injury. Analytical chemistry, 85(6), 3110-3117.
10. Chartuprayoon, N., Hangarter, C. M., Rheem, Y., Jung, H., & Myung, N. V. (2010). Wafer-scale fabrication of single polypyrrole nanoribbon-based ammonia sensor. The Journal of Physical Chemistry C, 114(25), 11103-11108.
11. Capone, S., Forleo, A., Francioso, L., Rella, R., Siciliano, P., Spadavecchia, J., &Taurino, A. M. (2003). Solid state gas sensors: state of the art and future activities. Journal of Optoelectronics and Advanced Materials, 5(5), 1335-1348.
12. Levitsky, I. A. (2015). Porous silicon structures as optical gas sensors. Sensors, 15(8), 19968-19991.
13. Lin, C.W., Chen, H.I., Chen, T.Y., Huang, C.C., Hsu, C.S., Liu, R.C., & Liu, W.C. (2011). On an indium–tin-oxide thin film based ammonia gas sensor. Sensors and Actuators B: Chemical, 160(1), 1481-1484.
14. Wang, Y., Jia, W., Strout, T., Ding, Y., & Lei Y. (2009). Preparation, characterization and sensitive gas sensing of conductive core-sheath TiO2-PEDOT nanocables. Sensors, 9(9), 6752-6763.
15. Hemant K, C., Ganesh N, S., Narendra V, B., & Vasant E, W. (2011). Synthesis of polypyrrole using ferric chloride (FeCl 3) as oxidant together with some dopants for use in gas sensors. Journal of sensor technology, 1(2),47-56.
16. Hamouma, O., Kaur, N., Oukil, D., Mahajan, A., & Chehimi, M.M. (2019). Paper strips coated with polypyrrole-wrapped carbon nanotube composites for chemi-resistive gas sensing. Synthetic Metals, 258, 116223.
17. Wang, C., Lei, S., Li, X., Guo, S., Cui, P., Wei, X., & Liu, H. (2018). A reduced GO-graphene hybrid gas sensor for ultra-low concentration ammonia detection. Sensors, 18(9), 3147.
18. Devi, R.S., Venckatesh, R., & Sivaraj, R. (2014). Synthesis of titanium dioxide nanoparticles by sol-gel technique. International Journal of Innovative Research in Science, Engineering and Technology, 3(8), 15206-15211.
19. Dighore, N., Dhonde, S., Gaikwad, S., & Rajbhoj, A. (2016). Synthesis of conducting polymer Polypyrrole-MoO3 nanocomposites. Moroccan Journal of Chemistry, 4(3), 4-3