# ELECTROSPUN FLEXIBLE NOBLE METAL DOPED $SNO_2$/POLYANILINE NANOFIBERS FOR HIGHLY SENSITIVE AND SELECTIVE HYDROGEN GAS SENSOR

Anand M. More1*, Hemlata J. sharma1, Subhash B. Kondawar1, Sunil P. Dongre2
[1]Department of Physics, Polymer Nanotech Laboratory, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur - 440033, India
[2]Department of Physics, Bhalerao Science College, Saoner, Nagpur - 441112, India

**A B S T R A C T**

**One-dimensional (1D) materials have attracted significant attention for device applications due to their unique optical, structural, electronic, magnetic and catalytic properties. Pure polyaniline (PANI) nanofibers based sensors are sensitive at room temperature but experiences disadvantages of high operating temperature, relatively poor solubility, selectivity, and stability. Pure metal oxide or doped metal oxide nanofibers based sensors are sensitive at high operating temperature but less sensitive at room temperature. In order to overcome these restrictions, PANI was functionalised or incorporated with nanoparticles of metal oxide, showing improved gas sensing characteristics. For the preparation of highly sensitive hydrogen gas sensor, we have fabricated a flexible 1D hybrid nanofibers composed of noble metal doped tin oxide/polyaniline by single-nozzle electrospinning and in-situ polymerization. The as-prepared metals Ag and Al doped $SnO_2$/PANI nanofibers were characterized by XRD and SEM-EDX. The results showed favourable interaction between PANI and metal doped $SnO_2$. Unlike other metal oxide nanofibers based sensors which are sensitive to many reducing and oxidizing gases and operate at a temperature of 350 °C or higher; these composites nanofibers based sensors are highly selective and sensitive to hydrogen gas with low detection range 1000-2000 ppm and operating at room temperature. The lower operating temperature enhances safety when dealing with hydrogen gas. Ag and Al doped $SnO_2$/PANI nanofibers were systematically compared for hydrogen gas sensing in terms of optimum operating temperature, response and recovery time. The sensing mechanism for these sensors is systematically explained in the present paper.**

**Keywords: Electrospinning, Nanofibers, Noble metal doped $SnO_2$/PANI, Gas Sensor, Hydrogen Gas.**

## 1. Introduction:

In recent years, the monitoring and controlling of various gases in the atmosphere become an important issue because of increasing pollution level in the atmosphere, global warming, drastic changes in the weather conditions, increase in the use of gas fuels such as Hydrogen, LPG. The purpose of monitoring could be achieved with the use of reliable, efficient, smart gas sensing device for all important gases. A gas sensor is a device which detects the presence of various gases in the area to be controlled. The presence of such gases beyond a particular limit may cause harm to human being and atmosphere. The key parameters of any gas sensor like sensitivity, selectivity, response time, stability, selectivity, reproducibility and reversibility solely depend on the material used for gas sensor [1]. The semiconducting metal oxide are the material of great use in the field of gas sensing, due to their ability for detecting various gases. Semiconductor based metal oxide sensors, whose resistivity can be modified by adsorption/desorption of the target species over the surface of the SMO proved beneficial because of their high performance, low cost and simple device design [2]. Recently, a lot of researches have been made in designing the hydrogen gas sensor using different fabrication techniques such as optical fiber, metal oxides

and MOSFET sensor. In metal oxide semiconducting sensors many materials such as ZnO, $SnO_2$, $TiO_2$, $WO_3$ are employed for hydrogen gas detection. Among them, n type metal oxide, $SnO_2$ has pulled the attention of the researchers significantly due to its excellent physico-chemical and electrical properties [3-7]. The use of $SnO_2$ has limitations for using it as hydrogen gas sensor since its working temperature is high enough to cause the explosion of hydrogen gas and consume more power for its operation [8]. The decoration or functionalisation of SMO can be done with doping of the noble metal nanoparticles such as Au, Ag, Pt, Pd etc. The dopant acts as catalyst by surface modification of SMO. The process of functionalisation could help in improving the sensor response which is also known as chemical sensitization [ 9-10][11-14]. Few researchers have suggested the use of CO and Mn nanoparticle doping which modifies the rutile structure of $SnO_2$, hence enhances the sensitivity of gas sensor towards hydrogen gas [15]. The effect of functionalization of nanoparticle of Pt have been observed on 3D hierarchical $SnO_2$ nanoflowers structure which causes the enhancement of the response of ethanol with better response and recovery time [16].

It is noticed that, when conducting polymers are added to the semiconducting oxide i.e. $SnO_2$ has the ability to improve the gas sensing properties, especially lowering the operating temperature at around room temperature. The additional benefit of conducting polymer PANI lies in ease of its chemical synthesis by chemical oxidative polymerization method. In addition to this, the ability to incorporate specific binding sites into the backbone of conducting polymers promises an improvement of selectivity and sensitivity of material [17-20]. Among all synthesized conducting polymers, polyaniline (PANI) is a typical p-type semiconductor and possessed distinctive redox property, controllable conductivity and good thermal stability. PANI could assist the sensing response towards many gases like $H_2$, CO, $NH_3$, when combined with $TiO_2$ or $SnO_2$ [21]. However, PANI is not as sensitive as metal oxides towards gas species and its poor solubility in organic solvents limits its applications [22]. Therefore, there has been increasing interest of the researchers for the preparation of nanocomposites based on PANI. The combination of organic and inorganic materials with different natures has been proposed as an effective approach to access complementary properties and synergetic effects and PANI/$SnO_2$ composite had excellent gas sensing properties [23].

In this paper, Ag and Al doped $SnO_2$ nanofibers are fabricated using electrospinning technique. As-prepared, nanofibers are dip-coated during the polymerization of the aniline. These nanofibers are utilized for the sensing of Hydrogen gas using in-house made sensing device. Al-SP and Ag-SP nanofibers are characterized using XRD, SEM and EDAX techniques. The sensing results are compared for Ag and Al functionalized $SnO_2$ polyaniline. The quick response, high sensitivity has been observed for Al doped $SnO_2$- Polyaniline (Al-SP) than Ag doped $SnO_2$- Polyaniline (Ag-SP). Low working temperature is observed for Ag-SP sensor. Sensitivity, response, selectivity study of the Ag-SP and Al-SP nanofibers has been carried out.

## 2. Experimental:

The chemicals needed for synthesis of nanofibers are a) Poly(vinylpyrrolidone) PVP M.W. 1,30,000gm/mol purchased from Sigma-Aldrich b) Silver Nitrate($AgNO_3$) c) Aluminum Nitrate($Al_2(NO)_3$) d) Stannous Chloride ($SnCl_2.2H_2O$) e) N-N Dimethyl formamide (DMF) f) Ethanol g) Camphor Sulphonic acid (CSA) were purchased as AR grade. All Chemical are used as obtained without further purification. All Solutions were made using double distilled water. The nanofibers were synthesized in two steps.

**2.1. Formation of nanofibers:** In a typical procedure to form Ag doped $SnO_2$ fibers, 0.2 gm of Stannous Chloride ($SnCl_2.2H_2O$) and 0.002gm of $AgNO_3$ (0.5M)2% by weight are dissolved in 2.3 ml (2.2 gm) Dimethyl formamide (DMF) and 2.6ml (4.4 gm) Ethanol. The solution is made homogenous by stirring it for half an hour with magnetic stirrer. 0.5 gm Poly(vinylpyrrolidone) PVP is added to the previously made solution, which was then stirred about 30-40 minutes. The viscosity of the solution was checked before pouring to 5ml syringe and loaded onto the Electro-spinning setup. The positive high voltage of 18 kV was

provided between the tip of the needle and the collector where the distance of 20 cm was kept between needle and collector. The collector was rotated with the speed of 1200-1500 rpm. The flow rate was maintained at 0.3 ml/h, maintained using computer control programmer. Nanofibers were peeled off and collected from collector were dried at about 70-80$^{o}$C for overnight. The dried nanofibers are calcined at 300$^{o}$C for 5 hour. Further calcined nanofibers are dip coated during the polymerization of aniline as follows [24].

**2.2 Polymarization of nanofibers:** For polymerization of Aniline, 5.5 gm of CSA (Camphor sulphonic acid) was taken in beaker A, containing 50 ml double distilled water and (0.2M) 0.9 ml aniline. In the other beaker B, (0.2M) 2.2gm Ammonium Peroxydisulphate (APS) is dissolved in 50ml double distilled water. Both the solutions were kept in thermostat at 5$^{o}$C for 4-5 hours. Solution of beaker B is added slowly to A with constant flow rate of solution of beaker B while dipping the Ag doped $SnO_2$embedded Polyaniline(Ag-SP) fibers. The similar process is repeated to form Al doped $SnO_2$ embedded polyaniline(Al-SP) nanofibers using Aluminum Nitrate as precursor [25].

**2.3 Characterization:**

The X-ray diffraction study for the crystal structure analysis was performed on PAN analytical diffractometer over the 2θ range from 20-80$^{o}$. The target used for X-ray diffraction was Copper(Cu) with λα = 1.53 A$^{o}$. Ag-SP and Al-SP nanofibers are studied for their surface morphological by using SEM technique. Surface study of the electrospun fibers was carried out with ZEISS SEM EVO-18. The operating potential was 5kV. The EDAX study was also carried out with ZEISS SEM-EDAX EVO-18.Ag-SP and Al-SP nanofibers formed by above mentioned method were employed for gas sensing purpose. Proper electrical contact was established by using silver electrode. The resistance change of the thin film was noted with the computerized resistance measurement software. The temperature of the nanofiber was controlled by automated heating system. The whole assembly is kept in cylindrical glass chamber which isolate the nanofiber from surrounding. The target gas is injected with the syringe of different volume. The change in the resistance of the nanofiber before and after injecting the gas at certain temperature was measured at different interval of time and recorded with the help of computer.

**3. Result and Discussion:**

**3.1. XRD analysis:** Ag-SP and Al-SP nanofibers were investigated and analyzed through X-ray diffraction. The X-ray diffraction pattern of 2θ against intensity is shown in Fig. 1.

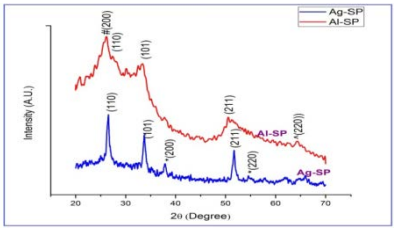



Fig.1: XRD pattern of Ag-SP and Al-SP nanofibers

The diffraction peaks are confirmed for $SnO_2$, Silver (Ag), Aluminum (Al) and polyaniline(PANI). Strong diffraction peaks are identified for $SnO_2$ at 2θ =26.6$^{o}$, 33.8$^{o}$, 52.4$^{o}$ corresponds to (110), (101),(211) which can be perfectly indexed as the tetragonal rutile structure of $SnO_2$ by comparing with JCPDS 41-1445. The prominent peaks of Ag are observed at 36.2$^{o}$, 44.4$^{o}$ corresponding to (111), (200) which are compared with JCPDS, silver file No. 04–0783. The prominent peak of Polyaniline is seen at 25.4$^{o}$ with (110). A characteristic peak for Aluminum (2 θ = 65 $^{o}$), corresponding to Miller indices (220) is observed and confirmed through JCPDS file no. 04-0787. XRD study of the nanofibers reveals the presence of the Ag and Al in $SnO_2$/PANI composite. Further the all peaks of Al And Ag are not seen in the XRD pattern, which may be because of low doping percentage of dopant (Ag/Al) and dominance of PANI in the composite of Al-SP and Ag-SP.

**3.2.EDX spectrum analysis:** The nanofibers Ag-SP and Al-SP are also analyzed using Energy Dispersive X- Ray Spectrum (EDX). *Fig 2(a) and 2(b)* shows EDAX spectrum for Al-SP and Ag-Sp respectively which reveals that the presence of elements Tin(Sn), Carbon(C), Nitrogen(N), Sulphur(S) and Silver(Ag) (5% of total weight) in Ag-SP and Tin(Sn), Carbon(C), Oxygen(O), Sulphur (S) and Aluminum(Al) (3% of total weight) in Al-SP. The EDX study indicates the formation Ag/Al doped $SnO_2$/PANI composite

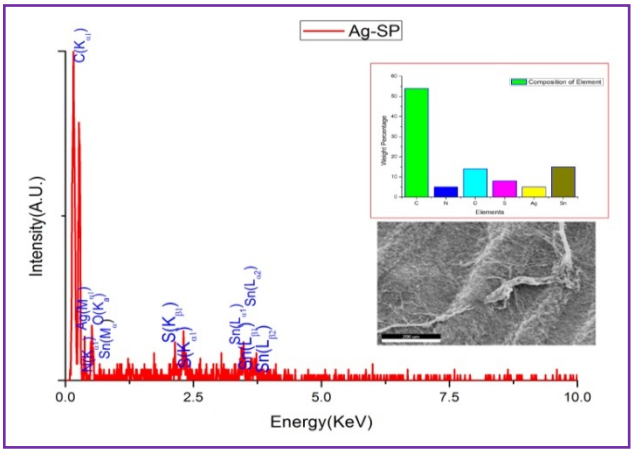



Fig.2 (a): EDAX pattern of Ag–SP nanofibers

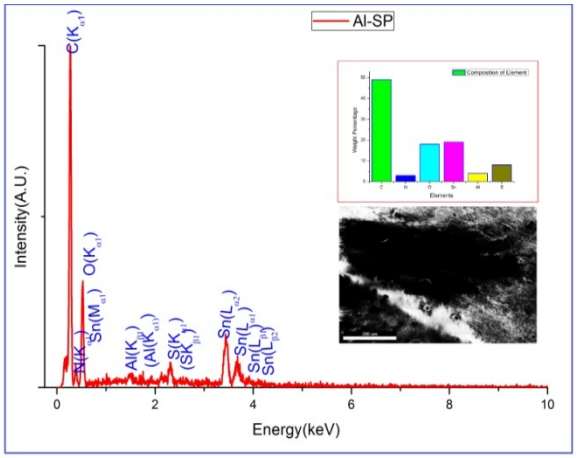



Fig.2 (b): EDAX pattern of Al-SP nanofibers

**3.3. SEM analysis of the Nanofibers**: The Ag-SP and Al-SP nanofibers are examined for SEM study. *Fig.3(a), Fig.3(b)* shows SEM micrograph of nanofibers. The figure elucidates formation of the nanofibers with nano-range. The diameter variance with the percentage distribution is shown in fig shown inset. It is evident from the inset figure that diameter of Ag-SP fibers is around 200-400 nm. The maximum probability of the diameter of Ag-SP is found in the range 200-300 nm. The diameter of Al-SP fiber is found to be 300-500 nm. It is seen from the diameter distribution that most of Ag-SP nanofibers has diameter in the range 300-400nm.

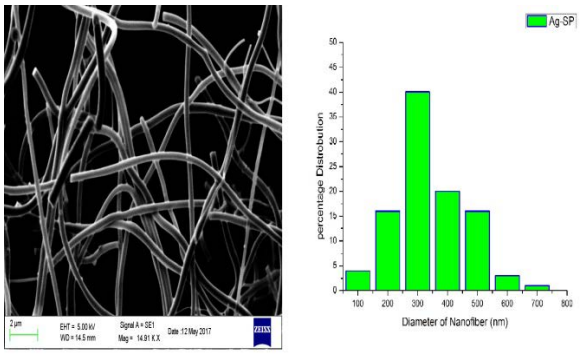



Fig.3 (a) : SEM images of Ag – SP nanofibers

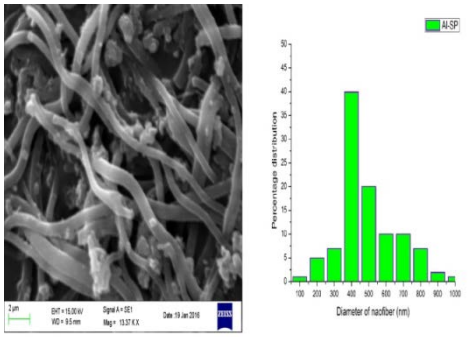
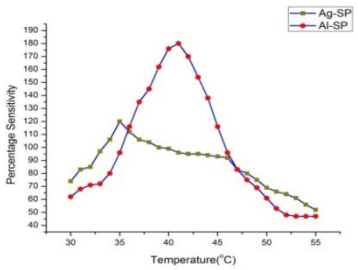



Fig.3 (b): SEM image of Al-SP nanofibers

**3.4 Gas Sensing of Nanofibers:** Ag-SP and Al-SP nanofiber films are used for the gas sensing study for hydrogen gas. Hydrogen gas in different concentration is allowed to interact with the nanofibers. The maximum percentage sensitivity [(Ra/Rg)-1) x100] is examined for the nanofibers for different temperatures. The variation of the percentage sensitivity with temperature is depicted in Fig.4 for Ag-SP and Al-SP. It has been observed that the maximum percentage sensitivity for Ag-SP and Al-SP for 1000 ppm each is at $35^0$C and $42^0$C respectively. Sensitivity study reveals that both the nanofibers are more sensitive around room temperature but Al-SP shows more sensitivity than Ag-SP at $42^0$C. The response study is shown in Fig.5. The response of Ag-SP and Al-SP have been studied at different hydrogen concentration at 1000 ppm and 2000 ppm. As shown in Fig.6, the response is seen to be increased for higher hydrogen concentration, since more active site would be engage in the reaction with hydrogen. The response time of Al-SP is 12 second and that of Ag-SP is 20 second. The recovery time of Al-SP is 15 second and that of Ag-SP is 33 second. It is evident from the gas sensing study that Al-SP is more reactive to hydrogen gas than Ag-SP.



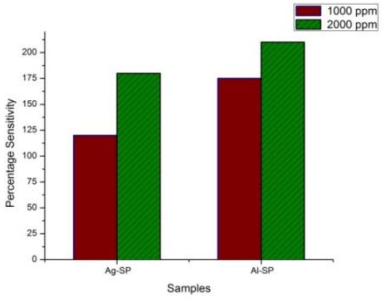
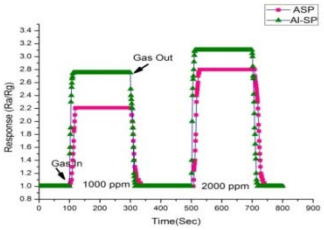




Fig.4: Percentage Sensitivity variation for Al-SP and Ag-SP nanofibers Fig.5: Response against con. of $H_2$ gas for Al-SP and Ag-SP nanofibers



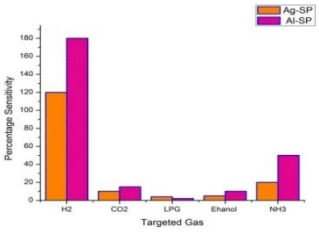




Fig.6: Response and recovery time for Al-SP and Ag-SP nanofibers Fig.7: Selectivity Study of Al-SP and Ag-SP nanofibers for various gases.

The nanofibers are also studied for selectivity towards hydrogen gas. Sensitivity of the nanofibers are investigated for Hydrogen($H_2$), Carbon monoxide(CO), Ammonia ($NH_3$),(LPG) and Ethanol. *Fig.7* indicates that both nanofibers are selective to $H_2$ gas but Al-SP is more sensitive and selective towards hydrogen gas as compared to Ag-SP.

The reactivity of $SnO_2$/PANI composite is enhancing by the chemical sensitization due to doping of Silver (Ag) and Aluminum(Al) nano-particle. The presence of Ag or Al contributes to the increase in the charge carriers. The conductivity thus improves with Al and Ag doped $SnO_2$/PANI composite. Further n type $SnO_2$ and p type PANI forms the **pn** junction at the interface of nanofibers. The barrier potential restricts the further flow of charge carrier, which could be increased by addition of Ag/Al elements into the matrix of $SnO_2$. The higher sensitivity of Aluminum may be due to its less atomic diameter as compared to Silver which best suits for substituting into the lattice of $SnO_2$ .

## 4. Conclusion:

From the present study of Ag-SP and Al-SP, it could be concluded that Al doping in $SnO_2$/PANI has more influence towards $H_2$ gas sensing than Ag doping. Both the nanofibers are reactive towards hydrogen gas around room temperature, but Al-SP is more sensitive. The response and recovery of Al-SP is quick as compared to Ag-SP. Both nanofibers show good selectivity of hydrogen gas against other gases. Thus Aluminum doped $SnO_2$/PANI composite is more suitable for hydrogen gas sensing at room temperature.

**Acknowledgements**

The authors are thankful to Head, Department of Physics, R.T. M. Nagpur University, Nagpur for providing SEM facility.

## REFERENCES

1. Ding B, Wang M, Yu J, Sun G, Gas Sensors Based on Electrospun Nanofibers, *Sensors*, , 9,2009, p 1610-1623.
2. Kim ID, Rothschild HL, Tuller HL, Advances and new direction in gas sensing devices, *Acta. Material*, 61(2013), p 974-1000.
3. Anand K, Singh O, Singh MP, Kaur J, Singh RC, Hydrogen sensor based on graphene/ZnO nanocomposite, *Sensors and Actuators B*, 195, 2014, p 409-415.
4. Ab Kadir R, Li Z, Sadek AK, Abdur Rani R, Zulfakar AS, Field MR, Electrospun granular hollow $SnO_2$ nanofibers hydrogen gas sensors operating at low temperatures., *Journal of Physical Chemistry C*, 118, ( 6), 2014, p 3129-3139.
5. Dutta D, Hazra SK, Das J, Sarkar CK, Basu S, Studies on p-$TiO_2$/n grphene

heterojunction for hydrogen detection, *Sensors and Actuators B* , (212) 2015, p 84-92.

6. Ou JZ, Yaacob MH, Campbell JL, Breedon M, Zadeh KK, $H_2$ sensing performance of optical fiber coated with nano-platelet $WO_3$ film, *Sensors and Actuators B*, 166,2012, p1-6.
7. Kim BJ, Yoon JH, Kim JS, Gas sensing characteristics of low powered duel MOSFET hydrogen sensor., *Materials Chemistry and Physics*,142, 2013 p 594-599.
8. Zhang D, Sun Y, Jiang C,Zhang Y, Room temperature hydrogen gas sensor based on palladium decorated tin oxide/molybdenum disulphide termary hybrid via hydrothermal route, *Sensors and Actuators B: Chemical* , 242, 2017, p15-24.
9. Matsushima S, Teraoka Y, Miura N, Yamazoe N, Elecronic interaction between metal additives and tin dioxide based gas sensor., *Journal of Applied Physics*, 1(27),1998, p 1798-1802.
10. Schweizer –Berberich M, Zheng JG, Gopel W, Barsen N, Pentia E, The effect of Pt or Pd surface doping on response of nanocrystaline tin dioxide gas sensor to CO, *Sensors and Actuators B*, 31,1996, p71-75.
11. Kotach A, Joon-Hyuk B., Sun-Woo C, One pot synthesis of Au doped $SnO_2$ and their gas sensing properties, *Sensors and Actuators B:Chemical*, 20, 2014, p 38-45.
12. Zang H, Li Z, Li L, Xu X, Wang Z, Wang W, Enhancement of hydrogen monitoring properties based on Pd-SnO2 composite nanofibers, *Sensors and Actuators B: Chemical*, 202, 2014, p111-115.
13. Joshi RK, Krishnan S, Yoshimura M, Ashok Kumar, Pd Nanoparticles and Thin Films for Room Temperature Hydrogen Sensor, *Nanoscale Res Letters*, 4 ,2009, p 1191–1196.
14. Yang Z, Miao YE, He S, A novel hydrogen peroxide sensor based on $Ag/SnO_2$ composite nanotubes by electrospinning, *Electrochimica Acta*, 4 2009, p117-123.
15. Lavanya M, Sekar C, Fazio E, Neri F, Development of a selective hydrogen leak sensor based on chemically doped $SnO_2$ for automotive application, *International journal of hydrogen energy*, 42(2017), p10645-10655.
16. Liu Y, Huang J, Wang J, Wang S, Pt nanoparticles functionalized 3D $SnO_2$ nanoflowers for gas sensor applications, *Solid State Electronics*, 130, 2017, p20-27.
17. Kim BJ, Oh SG, Han MG., Im SS, Synthesis and characterization of polyaniline nanoparticles in SDS micellar solutions, *Synthetic Materials*, , (122)2001, p 297-304.
18. MacDiarmid A, Epstein A, The concept of secondary doping as applied to polyaniline, *Synthetic Materials*,( 65) 1994, p103-116.
19. Kondawar SB, Patil PT, Agrawal SP, Chemical vapor sensing properties of electrospun nanofibers of polyaniline/ZnO nanocomposites, *Advance Material Letters*, 5(7),2014, p 389-395.
20. Chen J, Yang J, Yan X, Xue Q, $NH_3$ and HCl sensing characteristics of polyaniline nanofibers deposited on commercial ceramic substrates using interfacial polymerization, *Synthetic Materials*, 160 (23),2010, *p* 2452-2458.
21. Nasirian S, Moghoddam HM., Polyaniline assisted by $TiO_2/SnO_2$ nanoparticles as a hydrogen gas sensor at environmental conditions, *Applied Surface Science*, 328, 2015, p395-404.
22. Tai H, Jiang Y, Xi G, Yu J, Influence of polymerization temperature on $NH_3$ response PANI/$TiO_2$ thin film gas sensor, *Sensors and Actuators*, 129 2008, p319-326.
23. Sadek AZ, Baker CO, Zadeh K, Doped and dedoped polyaniline nanofiber based conductometric hydrogen gas sensor., *Sensors and Actuators A*, 139 2007, p53-57.
24. Patil GE, Kajale DD, Gaikwad VB, Preparation and characteristics of $SnO_2$ nanoparticles by hydrothermal route, *Interntional Nano-letters*, 2012, p 2-17
25. More AM, Sharma SJ, Kondawar SB, Dongre SP, Ag-$SnO_2$/Polyaniline composite nanofibers for low operating temperature hydrogen gas sensor, *Journal of Nanomaterials Nanoscience*, 4(1), 2017, p13-18.