Volume 15, Number 1, 2022. pp. 1-8

Jordan Journal of Physics

ARTICLE

Nanofibers of Palladium (Pd)-sensitized SnO_2 Encapsulated with Polyaniline for Effective Hydrogen Gas Sensing

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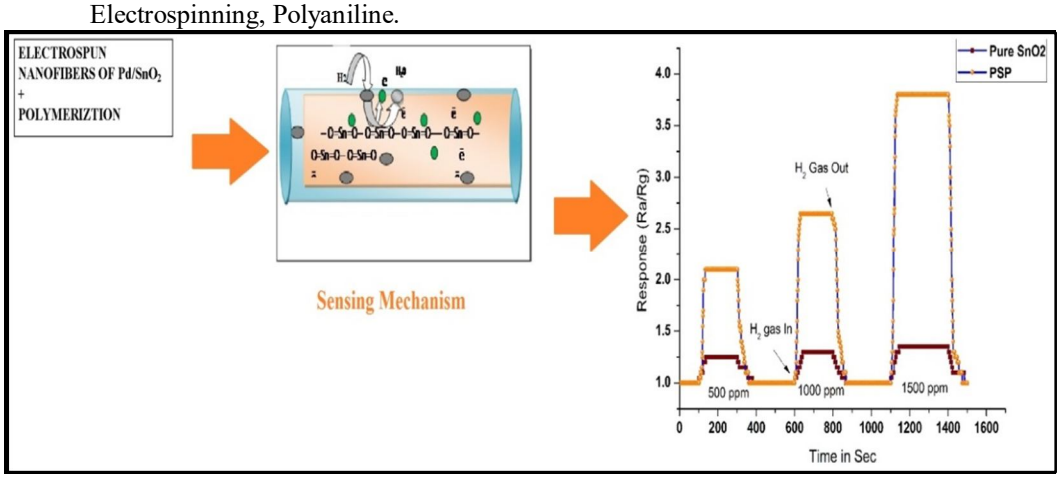
Doi: **https://doi.org/10.47011/15.1.1**

Received on: 01/08/2020; *Accepted on: 12/12/2020*

Abstract: In this paper, we have successfully synthesized Pd-doped SnO_2 nanofibers encapsulated with Polyaniline (PANI). The morphology of nanofibers was investigated using Scanning Electron Microscopy (SEM) technology. SEM study suggested that the diameter of Pd-doped SnO_2 encapsulated with polyaniline (PSP) nanofibers was found in the range 200-400 nm. The average diameter of PSP nanofibers was estimated using ImageJ software. XRD study of pure FIBRESSnO_2 and PSP nanofibers shows perfect matching of major peaks corresponding to Tin Oxide (SnO_2). EDAX pattern depicted weight percentage of constituent elements indicated the presence of Palladium (Pd) in nanofibers. The study revealed that PSP nanofibers were more sensitive as compared to pristine SnO_2 nanofibers. The working temperature of PSP nanofibers was found 32°C. The low working temperature provokes the use of PSP nanofibers as a promising hydrogen gas sensor. Response and recovery time of 34 seconds and 63 seconds respectively has been observed for PSP nanofibers. Palladium (Pd) could have played a major role in higher response towards hydrogen gas sensing. The mesoporous PSP electrospun nanofibers exhibited excellent response and recovery behavior, with much higher sensitivity to H_2 as compared with pure SnO_2 nanofibers. It could be understood that the high gas sensing performance of PSP nanofibers is obtained from the high surface area, with more activity at Pd active sites of nanofibers. Highly porous nature of electrospun nanofibers led to effective surface interaction between the hydrogen gas molecules and SnO_2 active site mediated by palladium for electron transfer through the matrix of nanofibers.

Keywords: Nanofibers, Hydrogen sensing, Pd-doped SnO_2 Polyaniline (PSP), Electrospinning, Polyaniline.



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Introduction

Today, we face drastic changes in atmospheric condition due to uncontrolled variation in the concentration of atmospheric gases like Hydrogen, CO_2, Methane, Oxygen and Nitrogen. Monitoring of these highly flammable and atmospheric gases is essential. Many techniques are employed for sensing these gases. The sensing devices use different parameters of sensing materials, such as their conductivity, optical property and mechanical strength. [1-2]. Wide variety of sensors, such as electrochemical sensor, optical sensor, chemo-resistive sensor is used for sensing important gases [3-4]. Semiconducting Gas Sensors are operated upon warming or heating metal oxides. Semiconducting Metal Oxides are used for measurement of gas concentration by measuring the electrical resistance of the device. Variation in the electron concentration over the surface of SMO in the presence of analyte gas is the key parameter in the detection of gas [5-6]. Sensors using semiconducting oxides (SMO) and Conducting Polymer are commonly used for the detection of gases, such as CO, CO_2, H_2, NH_3, H_2S, O_2, Ar and the presence of moisture in air [7]. However, high operating temperature, low selectivity, humidity dependence, low response and recovery time are the drawbacks of Semiconducting Oxides. It has been observed that reduction in the dimensions to nano-range can improve the ability of sensors of sensing gases to a great extent. Many researches indicate that doping of noble metals, such as Palladium (Pd), Silver (Ag), Gold (Au), Copper (Cu), Aluminium (Al) catalyses the sensor response of SnO_2 [6, 10, 11-14]. These metal elements provide more active site for the redox reaction between the target gas and the sensing material. SnO_2 is the most promising member in the series of semiconducting metal oxides, like ZnO, TiO_2, WO_3, In_2O_3, because it has considerable variation in the resistance in the presence of reducing gases like H_2, H_2S and oxidizing gases like NH_3, O_2 [15-19]. Electrospun nanowires of SnO_2 could provide larger surface area for interaction with target gas. Pd-functionalized nanostructures exhibited a dramatic improvement in sensitivity toward oxygen and hydrogen due to the enhanced catalytic dissociation of the molecular adsorbate on the Pd nanoparticle surfaces and the subsequent diffusion of the resultant atomic species to the oxide. Further, another approach suggested that the receptor for the analyte gas has been drastically modified by the introduction of foreign receptors, in particular Pd and Ag, on the surface of SnO_2 [9]. Pd and Ag promoters form oxides in the presence of air. These oxides of Pd or Ag interact with the SnO_2 electrospun nanofibers and form an electron-deficient space-charge layer which contributes much to promoting the gas sensitivity. Electrospinning is an important technique to obtain nanofibers of 1D hierarchical formats with enhanced reactivity due to availability of active site for the reaction of the gas over the matrix of nanofiber [20]. Polyaniline (PANI)-based SMO has a relatively high sensitivity to gases due to its conductive nature.

In this paper, we have interpreted the sensing response of Pd-doped SnO_2 embedded polyaniline (PSP) to the hydrogen gas at low temperature.

Experimental Details

Preparation of Pd-doped SnO_2 Embedded Polyaniline Nanofibers (PSP)

Fig. 1 shows the schematic diagram of preparation of nanofibers of Pd-doped SnO_2 encapsulated with Polyaniline [21]. In the first step, 0.2 g of Stannous Chloride ($SnCl_2.2H_2O$) and 0.002g of $PdCl_2$ (1% by weight) were dissolved in 2.3 ml (2.2 g) Dimethyl formamide (DMF) and 2.6ml (4.4 g) ethanol solution. The resulting gel - solution was stirred for half an hour with magnetic stirring to get proper viscosity. Afterwards, 0.6g Poly (vinylpyrrolidone) PVP was added to the solution. The solution was stirred for the next 30-35 minutes to attain proper viscosity. For electrospinning, the solution was firstly filled in 10ml syringe. The potential of 18 kV was provided between the tip of the spinning nozzle and the collector which were kept at a distance of 25 cm apart. The solution flow rate was kept at 0.5 ml/h. Nanofibers collected on the electrode were dried at about 70-80°C overnight. The dried nanofibers were peeled off. The dried nanofibers were calcined at 350 °C for 5 hours. In the second step, calcined nanofibers were dip-coated during the polymerization of aniline. The coated fibers were dried at about 100 °C. The nanofibers so formed were used for gas-sensing purposes.

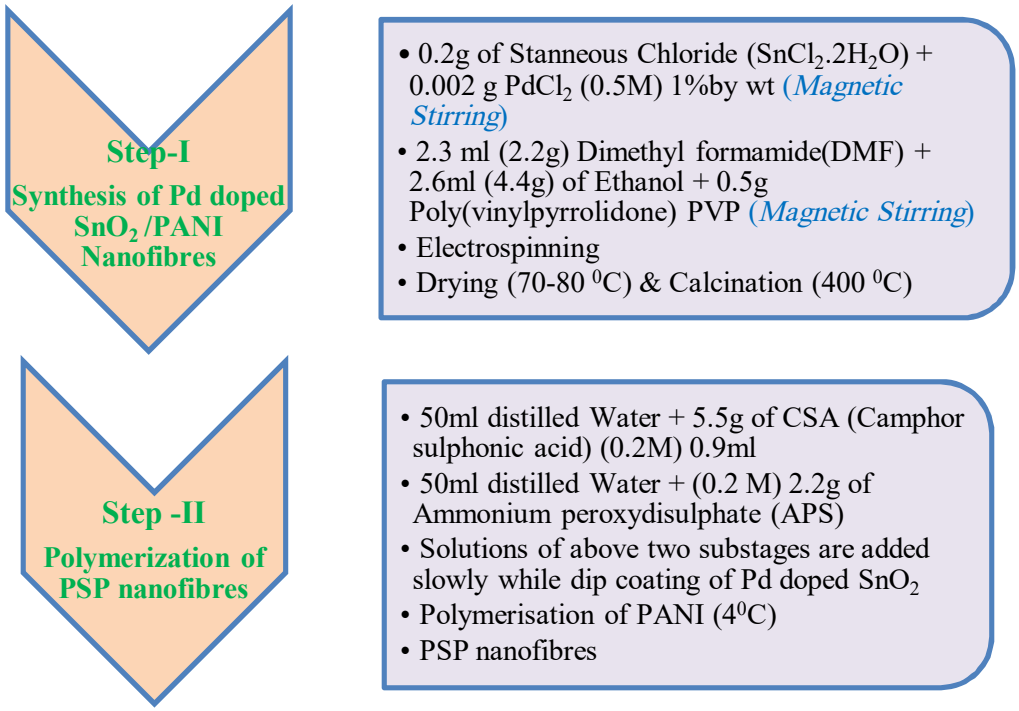

FIG. 1. Synthesis of Pd-doped SnO_2 encapsulated with PANI (PSP) nanofibers.

TABLE 1. List of chemicals with details of suppliers.

S.N.	Chemicals	Supplier	Purification Grade
1.	Poly(vinylpyrrolidone)PVP(M.W. 130,000gm/mol)	Sigma-Aldrich	A.R.
2.	Silver Nitrate($AgNO_3$)	HI- MEDIA	A.R.
3.	N-N Dimethylformamide (DMF)	HI- MEDIA	A.R.
4.	Ehanol(C_2H_5OH)	HI- MEDIA	A.R.
5.	Camphor Sulphonic acid (CSA)	HI- MEDIA	A.R.

Results and Discussion

SEM Analysis of the Samples

The SEM micrographs of pure SnO_2 and Pd-doped SnO_2 polymerized by aniline are analysed using Scanning Electron Microscopy (SEM), (Carl Zeiss Model EVO-18, JSM-7600F) which depict that the diameters of the nanofibers of pure SnO_2 and Pd-SnO_2-PANI (PSP) composite fibers are about 400-500 nm. The average diameters were estimated using ImageJ software. Many fibres were chosen at different positions of nanofibers for collecting data for diameter. Fig. 2a and Fig. 2b show the typical SEM images of pure SnO_2 and Pd-SnO_2/ PANI (PSP) composite nanofibers, respectively. The diameter distribution of PSP fibers also shown in the adjoining Fig. 2a and Fig. 2b indicated that most probable diameters of nanofibers are found in the 200-400 nm range. SEM image reveals the hierarchical branched structure of PSP nanofibers. The trend to increase the diameter of PSP nanofibers after polymerisation is because of encapsulation of Pd-doped SnO_2 by polyaniline (PANI).

XRD Analysis of the Samples

XRD analysis is the plot between number of counts having Arbitrary Unit (AU) and diffraction angle (2θ). Fig. 3a shows the XRD pattern for pure SnO_2 and Pd-doped SnO_2 encapsulated with PANI (PSP) nanofibers. The major diffraction peaks are confirmed for SnO_2 and PSP nanofibers with standard data. The diffraction peaks have been identified for SnO_2 at 2θ =26.6^o, 33.8^o, 52.4^o corresponding 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 peak of Polyaniline is seen at 25.4^o with (110). A small shift in peak positions has been observed for Pd-doped SnO_2 /PANI (PSP) nanofibers. The peaks of Palladium (Pd) are not prominent because of very little concentration of dopent Pd

in the sample. The constituent elements Pd, Sn, N, O, C have been detected by EDAX pattern which is clearly seen in Fig. 3b. The crystal size of SnO_2 molecule has been estimated using Debye-Scherrer's relation for grain size. Mathematically, Debye-Scherrer relation is given as:

$$\tau = \frac{0.9\,\lambda}{\beta\, Cos\theta}$$

where, τ = Crystal size, λ = X-ray wavelength used for diffraction ($\lambda = 1.53$ Å), β = Full width at Half Maxima (FWHM), θ = Diffraction angle. From Table 2, it is evident that the average crystal size of SnO_2 is found to be 5.60nm.

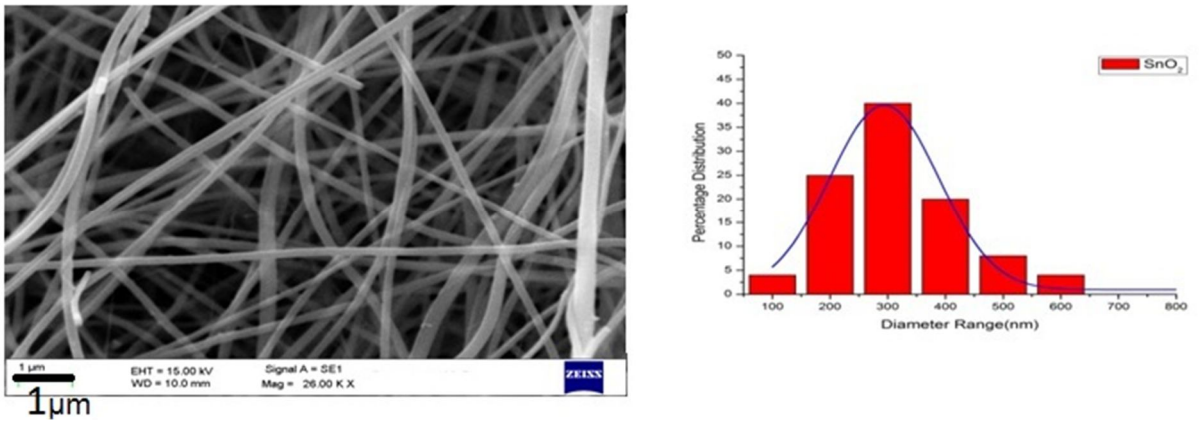

FIG. 2a. SEM image and diameter distribution of SnO_2 nanofibers.

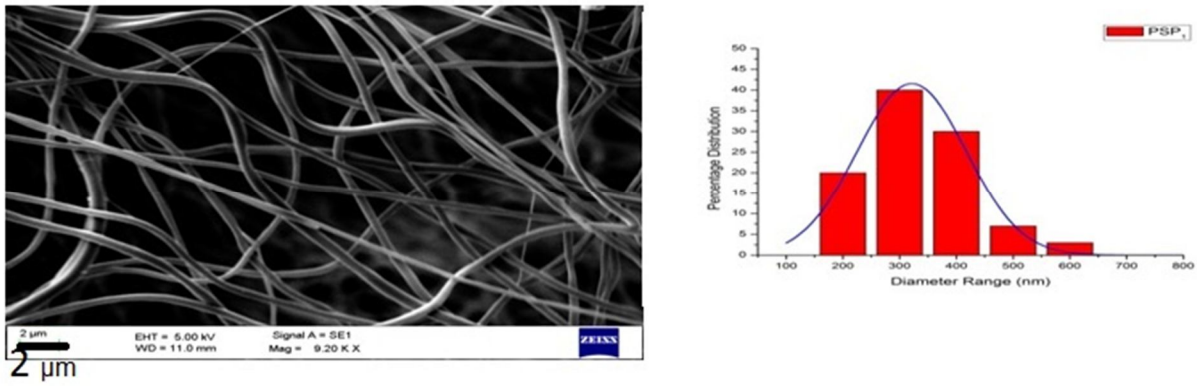

FIG. 2b. SEM image and diameter distribution of Pd-doped SnO_2 encapsulated with PANI (PSP) nanofibers.

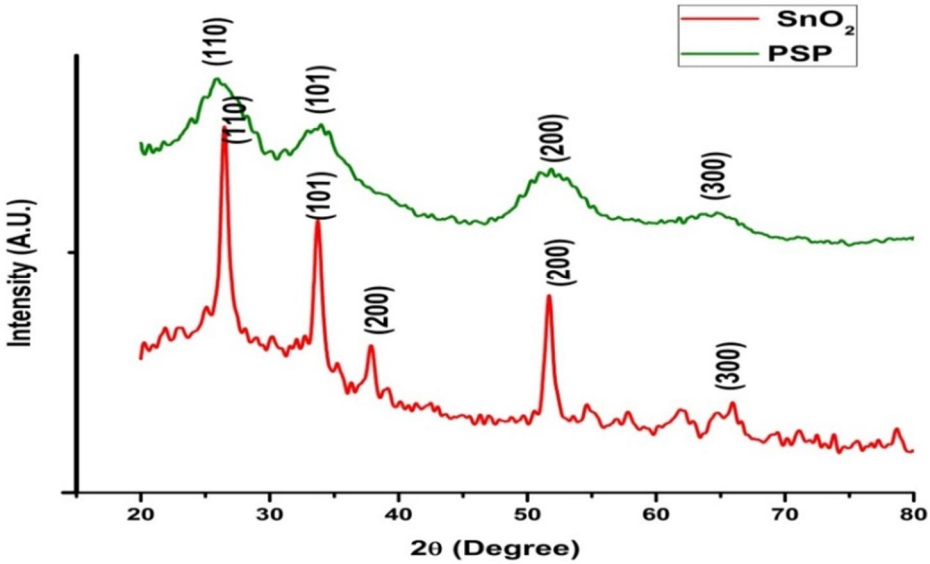

FIG. 3a. XRD pattern for pure SnO_2 and Pd-doped SnO_2 encapsulated with PANI (PSP) nanofibers.

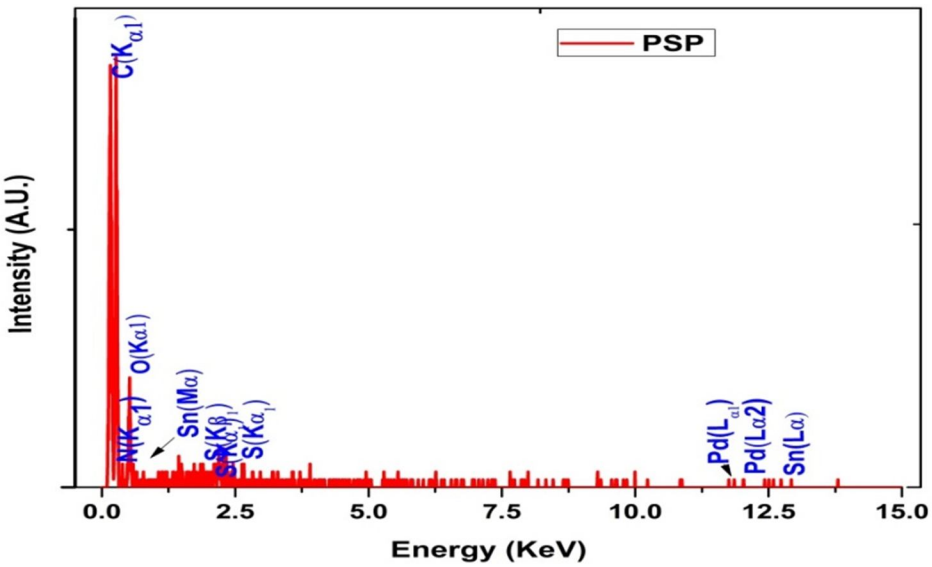

FIG. 3b. EDAX pattern of Pd-doped SnO_2 encapsulated with PANI (PSP) nanofibers.

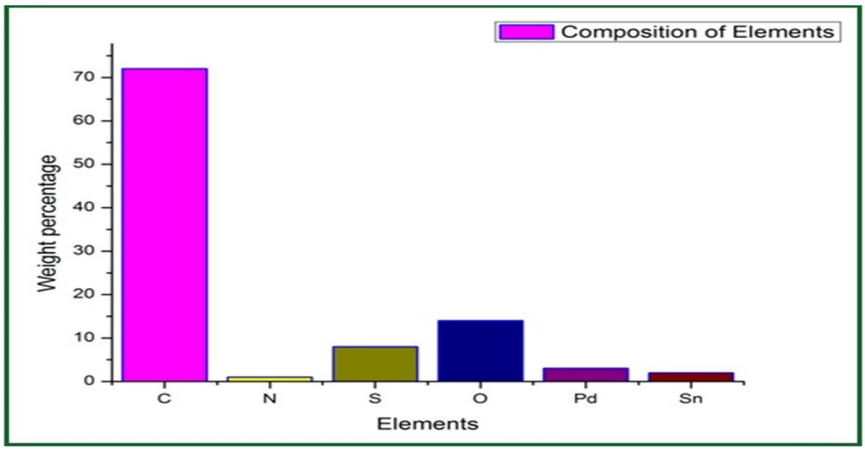

FIG. 3c. Composition of elements of Pd-doped SnO_2 encapsulated with PANI (PSP) nanofibers from EDAX pattern.

XRD and SEM study showed that nanocrystalline SnO_2 had been synthesized. SEM images estimate size of nanofibers of SnO_2 and PSP to be in the range of 200-400 nm. It is evident from the different sizes of nanofibers calculated from Debye-Scherrer's formula and SEM microgram that nanofibers are of multi-layered, polycrystalline nature. Further encapsulation of Pd-doped SnO_2 nanofibers by polyaniline (PANI) shows an enhancement in diameter.

TABLE 2. Determination of crystal size of SnO_2 by Debye- Scherrer formula.

Diffraction Angle (2θ)	Miller Indices (h k l)	Interplanar Spacing ($\tau = \frac{0.9\,\lambda}{\beta\, Cos\theta}$) for Each Plane (nm)	Mean Size for SnO_2 Crystal (nm)
26.56	110	5.34	5.60
33.7	101	5.04	
37.82	200	4.8	
51.7	211	7.23	

Gas Sensing of Samples

Pristine SnO_2 and PSP nanofibers were utilized for hydrogen gas sensing. The percentage sensitivity, which is given as {[(Rg-Ra)/Ra] x 100}, is evaluated for 1000 ppm of hydrogen gas and plotted against temperature. The variation of percentage sensitivity with temperature is shown in Fig. 4. Nanofibers were found to have maximum sensitivity at 32°C for PSP than pristine SnO_2. The sensitivity rises to

170% of its initial conductivity value. The higher sensitivity may be attributed to the presence of Palladium (Pd) in the PSP nanofibers. Pd nanoparticles form oxides in the presence of air. These oxides of Palladium (Pd) interact with the SnO_2 electrospun nanofibers and form an electron-deficient space-charge layer which contributes much to enhancing hydrogen gas sensitivity. The response (Ra/Rg) of the SnO_2 and PSP plotted against time shows that response time and recovery time are 34 seconds and 63 seconds, respectively. Fig. 5 shows the response of nanofibers for 500 ppm, 1000ppm, 1500ppm of hydrogen gas. The low-temperature high sensitivity of the PSP nanofibers is due to a large spill-over of the Pd nanoparticles. The variation of the response with the concentration of hydrogen gas at different ppm values reveals maximum response for PSP over pristine SnO_2. PSP has been studied for selectivity using different gases for 1000 ppm at 35 °C. It has been observed that PSP is more selective towards hydrogen gas as compared with NH_3, ehanol, LPG and CO_2 gases.

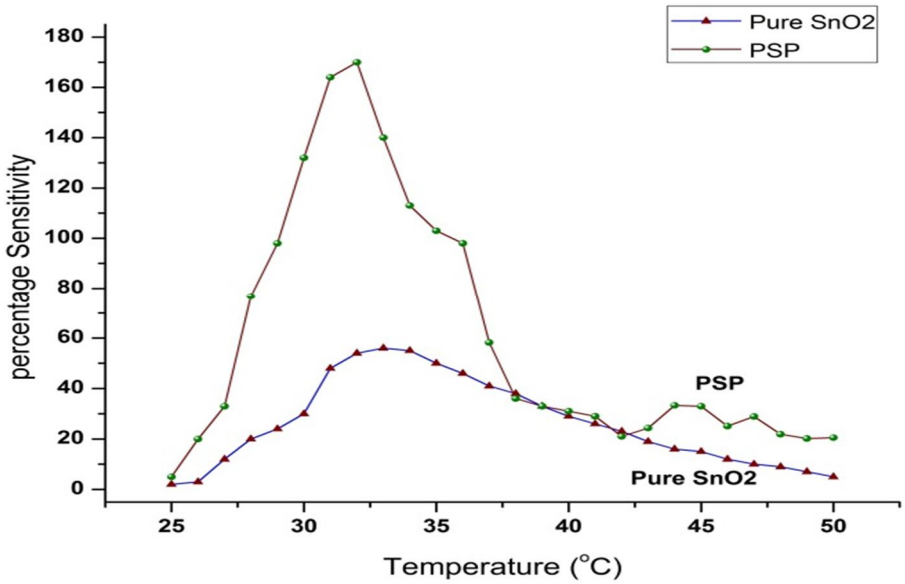

FIG. 4. Sensitivity study of pure SnO_2 and Pd-doped SnO_2 encapsulated with PANI (PSP) nanofibers for hydrogen gas.

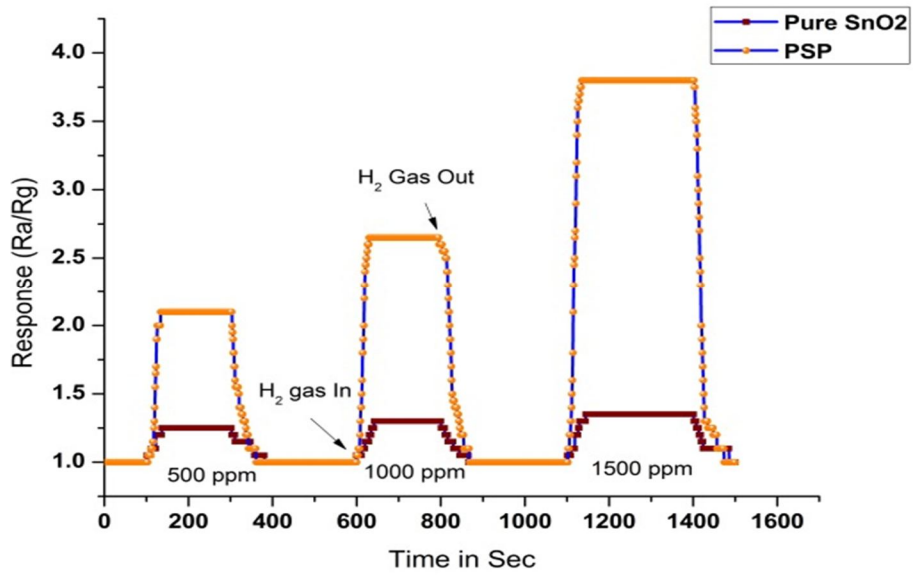

FIG. 5. Response study of pure SnO_2 and Pd-doped SnO_2 encapsulated with PANI (PSP) nanofibers for different parts per million (ppm) of hydrogen gas.

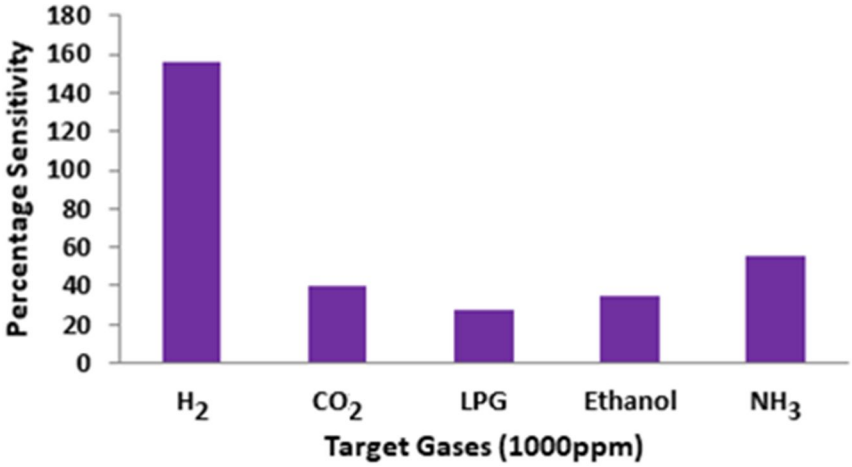

FIG. 6. Selectivity study of Pd-doped SnO_2 encapsulated with PANI (PSP) nanofiber for 1000 ppm of different gases.

Conclusions

PSP nanofibers have been synthesized successfully. The formation of PSP nanofibers includes two steps. In the first step, Pd-doped SnO_2 nanofibers were synthesized, followed by step two in which dip coating of Pd-doped SnO_2 nanofibers is achieved during polymerization of aniline. The XRD study of the nanofibers indicates the formation of crystalline SnO_2 with an average grain size of 5.60 nm. The prominent peaks of SnO_2 show good agreement with the standard peaks from JCPDS file. EDAX pattern depicts the composition of constituent elements. SEM images with diameter distribution of pristine SnO_2 and PSP nanofibers indicate that the average diameters are approximated to 200-400 nm. The average diameter of nanofibers is different from crystal size of SnO_2 due to poly-crystalline nature of nanofibers. The remarkable sensitivity of PSP nanofibers for hydrogen gas has been observed near 32 °C. This indicates that PSP could be used to sense hydrogen gas efficiently near room temperature. The response and recovery times of 34 and 63 seconds respectively promote the practical use of PSP nanofibers for hydrogen gas sensing. The higher percentage of Pd doping could enhance the sensor response. Selectivity of PSP is outstanding for hydrogen gas compared with other gases, like NH_3, CO_2, ethanol vapours. Future work with PSP nanofibers may be advanced with multiple directions, such as different doping percentages of palladium, different polymers for conductivity and modeling of sensitivity study.

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