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Accelerated Hydrogen Gas Sensing of SnO_2 Embedded Polyaniline Nanofibers with Doping Pd or Ag Near Room Temperature

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In the present paper, Ag doped SnO_2 embedded Polyaniline (ASP) nanofibers and Pd doped SnO_2 embedded Polyaniline (PSP) nanofibers have been synthesized successfully. These nanofibers are prepared through the process of electrospinning. ASP and PSP nanofibers have investigated through XRD, EDAX and SEM. The major peaks of the XRD pattern showed perfect matching with JCPDS 41-1445 and confirm rutile nature of SnO_2. Energy dispersive study showed composition of elements constituting ASP and PSP nanofibers. SEM images for different doping concentration of Ag and Pd have been obtained which indicate that nanofibers in the range of 100-700 nm are formed. The diameter distribution of SEM images depicted that most probable diameter of the nanofibers is in the range of 300-400nm. ASP and PSP showed promising results for detection of hydrogen gas. Percentage sensitivity variation with temperature showed the working temperature of around 35^oC for all ASP and PSP nanofibers. Response and recovery studies showed response time and recovery time 12-18 second and 20-32 second respectively. Further Pd doping enhances reactivity of SnO_2 nanofibers as compared to Ag doping into SnO_2 matrix. PSP nanofibers are more selective to hydrogen gas when compared with other atmospheric gases and vapours. The hydrogen gas sensing is assisted through sensitization of Pd decorated SnO_2 surface and hierarchical structure of nanofibers.

Keywords: Electro spinning, Noble metal doping, Nanofibers, Polymers, Sensors, Semiconducting oxides

1 Introduction

Hydrogen is one of the cleanest energy sources with highest calorific value (120-142 x 10^3 kJ/g) and near zero greenhouse gas emission. Major challenges lie in storage because it requires high pressures, low temperatures or chemical processes to be stored compactly. Hydrogen needs to be stored in containers in automotive vehicles using hydrogen fuel cells. Therefore, monitoring the leakage of hydrogen through such storage vehicles is must to ensure normal operations of automotive. Thus continuous monitoring is required to improve the overall safety of the passengers as well as the vehicle. Many sensor devices using different technologies are employed for the purpose of hydrogen gas sensing which includes Semiconducting Metal Oxides (SMO), Electrochemical Cell, Catalytic and Thermal Conductivity. Miniaturization of electronic devices have played vital role in sensing technologies for enhancement of sensor response, reproducibility, working temperature. Application of advanced fabrication technologies has enabled sensor miniaturization and development of sensor arrays with enhanced selectivity and sensitivity.[1]

Wang et al have suggested that semiconducting oxides viz. SnO_2, ZnO, TiO_2, In_2O_3 can be employed for hydrogen gas detection.[2-3]SMO has represented an appealing class of materials in the field of gas sensing because of it's sensitivity to most of the gases, low costing and ease of synthesis with simple techniques.[4-7] Investigation on critical issues of sensitivity, response time, selectivity, recovery and mechanical strength suggested that nanostructured one/ two dimensional semiconducting oxides(SMO) shows better sensing performance compared with thick or thin film structures.[8-9] Few researchers used different synthesis techniques including magnetic sputtering, spray pyrolysis, thick films, thin films, inter-digited-electrodes (IDE) thin films and electrospun nanofibers.[10-12] Enhancement in the detection ability is

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observed by doping semiconducting oxides with noble metals such as Silver(Ag), Gold(Au), Platinum (Pt), Palladium(Pd).[13-16] Noble elements have been suggested for improvement in response for hydrogen gas and declination in working temperature.[17-20] Many researchers have identified conducting polymers viz. Polypyrrole(PPy), Polyaniline (PANI), Polythiophene (PTh) and Polyvinyl-alcohol (PVA) to improve the conductivity of the SMO.[21-22]Polymer possesses high sensitivity, good mechanical strength but low response and recovery times. Redox reaction (Protonation- deprotonation) is thought to play an important role in providing conductivity in case of Polyaniline. Many researchers have suggested that hierarchical structures of nanowires (NW) of SnO_2 doped with Nobel metals like Pd, Au and Ag exhibit better response over nanowire structure of SnO_2. [23-24] Ding et al suggested that 2-D nanostructureof nanofibers/NW possess high surface to volume (S/V) ratiocould accelerate reactivity of the target gas with the matrix of the sensing material of SMO.[25]Joong et al found that the hollow mesoporous architecture affords a large specific surface area, which can provide more reaction active sites of sensing materials significantly.[26]

Thus enhanced sensing properties can be obtained by surface modification which is known as decoration or functionalization of the SMO. Functionalization is achieved either by addition of noble atom nanoparticles (NPs) which helps in adsorption of the analyte gas onto the surface of the SMO or by rearrangement of surface energy levels of SMO. Sensing results are elevated further with the use of nano-range particle (< 100nm) in lower concentration (< 10 % by wt), high dispersion of the gas along the surface matrix to promote catalytic activity without loss of original functionality of host SMO.[27-28]

2 Materials and Methods

The chemicals used for synthesis of ASP and PSP nanofibers were A.R. grade. All chemicals have been used as supplied without further purification process. All the solutions were made using double distilled water.

The typical two-step process is followed for synthesis of Ag doped SnO_2 /PANI nanofibers. In the first step, Ag doped SnO_2 electrospun nanofibers are prepared. 0.2g Stannous Chloride ($SnCl_2.2H_2O$) and 0.002g $AgNO_3$ (0.5M)1% by weight are dissolved solution containing 2.3 ml (2.2 gm) Dimethyl formamide(DMF) and 2.6ml (4.4 gm) Ethanol. This solution is stirred for half an hour with magnetic stirring. The PVP is used as carrier polymer for electrospinning which provide proper viscosity to the gel solution. PVP helps in drawing the fibers from the solution which can be easily removed by little heating of the fibers. 0.5 g Poly(vinylpyrrolidone) PVP is added to above solution and stirred for next 30-40 minutes. The solution with proper viscosity is filled in 10ml syringe and loaded onto the Electrospinning setup. The fibers are collected on cylindrical conductor and dried at about 70-80^{0}C for overnight. The dried nanofibers are calcined at 300^{0}C for 4 hour.

In the second step, calcined SnO_2 nanofibers are employed for dip coating during polymerization of Aniline. Polymerization is done with 5.5 gm of CSA (Camphor Sulphonic Acid), 50 ml double distilled water and (0.2M) 0.9 ml aniline in beaker A. In another beaker B, (0.2M) 2.2gm Ammonium Peroxydisulphate (APS) is dissolved in 50ml double distilled water. Both the solutions in beaker A and B were maintained at 5^{0}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 fibers. The coated fibers are dried over-night at 100 ^{0}C . The fibers after calcinations at 300^{o}C are used for gas sensing study.

Similar synthesis route is used for Pd doped SnO_2 / PANI nanofibers with 0.002gm $PdCl_2$ (0.5M) instead of $AgNO_3$.

3 Result and Discussions

As synthesized nanofibers of ASP and PSP are investigated for the morphological characterization using XRD, SEM and EDAX. The nanofibers were used for hydrogen gas sensing.

3.1 XRD Analysis

The X-Ray diffraction analysis has been obtained on PAN analytical diffractometer over the scanning angle 2θ range 10^0-70^0. Strong diffraction peaks observed at 2θ =26.6^0, 33.8^0, 64.6^{0}corresponds to lattice planes (110), (101), (211) of SnO_2 which can be perfectly indexed as the tetragonal rutile structure of SnO_2 by comparing with JCPDS 41-1445. The planes *(200),* (111) and *(220) at corresponding angle 2θ =38.4^0, 52.4^0 represent less prominent peaks of SnO_2. The prominent peak of Polyaniline coincides with SnO_2 at 25.4^0 with (110). Figure 1 depicts the XRD pattern of SnO_2, ASP and PSP nanofibers with prominent peaks.

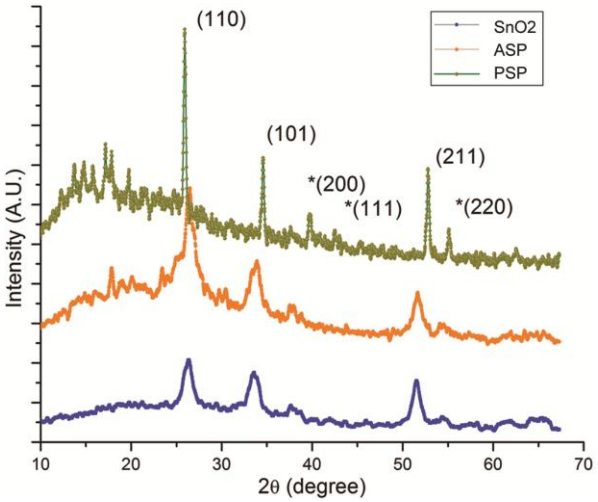

Fig. 1 —X-Ray diffraction pattern of SnO_2, Ag doped SnO_2 embedded Polyaniline (ASP) and Pd doped SnO_2 embedded Polyaniline (PSP).

Table 1 — Minimum diameter of nanofibers from SEM images

S. N.	Name of Nanofiber	Minimum diameter of Nanofiber	Maximum diameter of Nanofiber
1.	ASP_1	72 nm	402 nm
2.	ASP_2	74 nm	376 nm
3.	ASP_3	80 nm	562 nm
4.	PSP_1	96 nm	519 nm
5.	PSP_2	106 nm	467 nm
6.	PSP_3	125 nm	620 nm

3.2 SEM Analysis

The diameter of ASP and PSP nanofibers was investigated by SEM technique. It is confirmed from SEM study that all nanofibers are in 72-620 nm range. The diameter distribution of all nanofibers is performed for confirmation of the most probable diameter distribution of nanofibers.The minimum diameter of the nanofiber found in the SEM images of ASP and PSP nanofibers are mentioned in Table 1. The diameters are found from SEM images using imagej software. Hence the diameter range of ASP nanofiber and PSP nanofiber is 72-562 nm and 96-620 nm respectively.

Small increase of diameter is observed if doping percentage of silver increases in nanofibers.As the doping of Silver (Ag) increased from ASP_1 to ASP_3, the minimum diameter of nanofiber is increased from 72nm to 80 nm. Similarly the minimum diameter of PSP nanofiber is increased from 96 nm to 195 nm, as the doping percentage increased. The table shows the same trend of variation of diameter for both nanofibers. Figure 2 (a-f) shows SEM images of nanofibers of ASP and PSP. The diameter distribution of nanofibers is represented with inset graph of each diagram. Energy Dispersive (EDAX) study of the nanofibers shows the presence of Silver (Ag) and Palladium (Pd) with other elements such as Carbon (C), Nitrogen(N), Oxygen (O) and Tin (Sn). The composition of elements for ASP and PSP nanofibers is shown in the Fig. 3 (a-b).

3.3 Hydrogen Gas Sensing

Ag/Pd doped SnO_2 embedded PANI nanofibers are employed for hydrogen gas detection. For sensing, hydrogen gas with different concentration at ppm level is mixed in air. The variation of conductivity of ASP and PSP are recorded at different concentrations and temperatures. The response and recovery time, sensitivity and selectivity of nanofibers for hydrogen, various atmospheric gases and vapours are studied. Figure 4 shows variation of percentage sensitivity versus temperature of the nanofibers. Lowest sensitivity is observed for SnO_2 and highest sensitivity for Pd (3% by weight) doped SnO_2 embedded PANI i.e. PSP_3 nanofibers. Highest percentage sensitivity for ASP and PSP nanofibers has been observed between temperatures 30^0 C - 40^0C. The doping of Silver (Ag) and Palladium (Pd) enhances the conductivity of the nanofibers, hence enhances reactivity to the target gas. Hydrogen being the reducing gas releases electron in SnO_2 lattice. The presence of hydrogen gas in the surrounding can be detected as the rise in conductivity of nanofibers. It has been observed that hierarchical structures of nanofibers reduce resistivity by providing shorter route for flow of electrons. Thus hierarchical structures of electrospun nanofibers exhibit high response to target gas. Further presence of conducting polymer like Polyaniline (PANI) on the surface of SnO_2 nanofibers supports speedy passage for electron, which could contribute for higher sensitivity of PSP and ASP nanofibers. Quick response and faster recovery of the ASP and PSP nanofiber is noticed. Nanofibers shows quick response time of 12 sec- 18 sec. The recovery time of nanofibers is found to be 20 sec- 32sec. Figure 5 & 6 show that response curve for ASP & PSP nanofiber for 500 ppm, 1000ppm and 1500ppm of hydrogen gas. The Fig. 5 & 6 depicted higher response for nanofibers containing Pd in comparison to Ag at different concentration of hydrogen gas. Higher response to the Pd doping in SnO_2 lattice could be due to spillover effect associated with Palladium.

It has been observed that palladium (Pd) enables the dissociation of hydrogen molecule into hydrogen

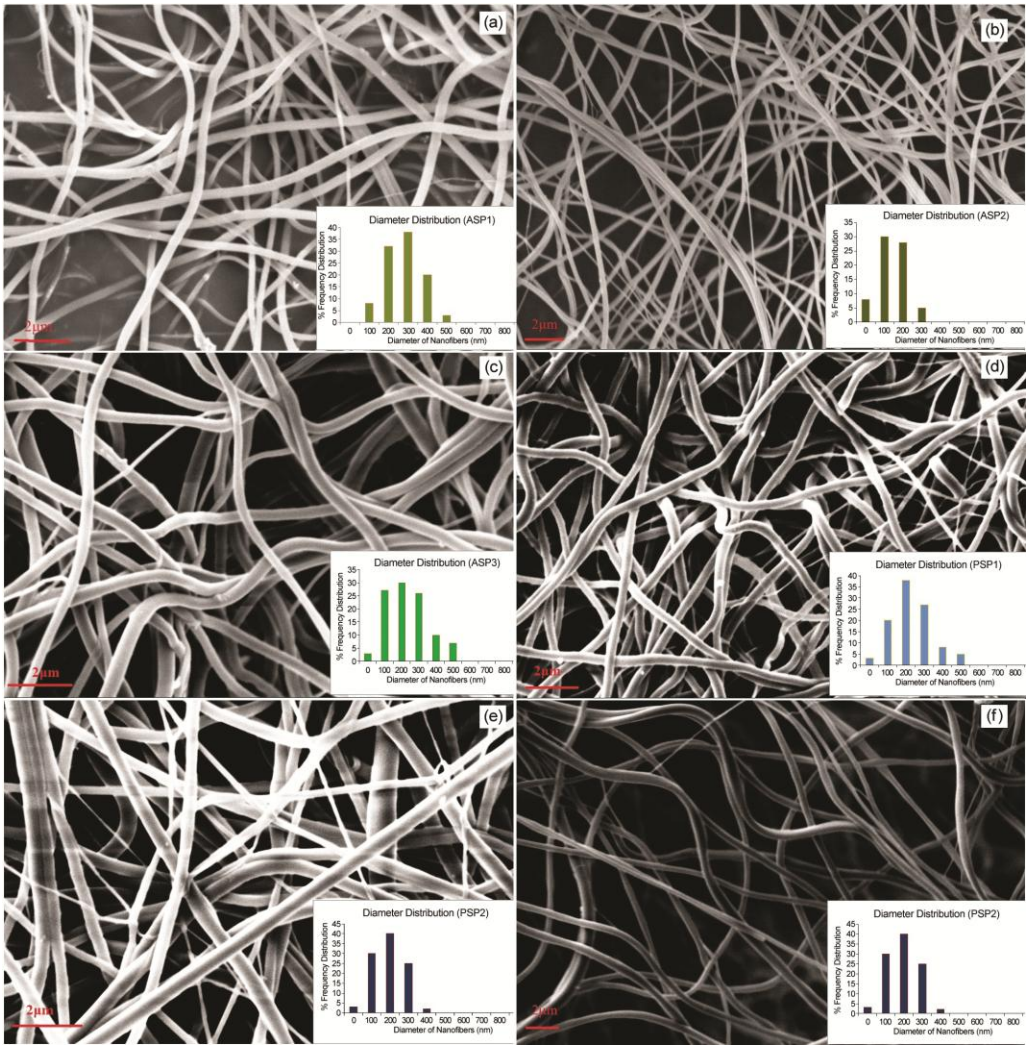

Fig. 2 — (a) SEM Image of ASP_1 nanofibers, (b) SEM Image of ASP_1 nanofibers, (c) SEM Image of ASP_3 nanofibers, (d) SEM Image of PSP_1 nanofibers, (e) SEM Image of PSP_2 nanofibers, and (f) SEM Image of ASP_3 nanofibers.

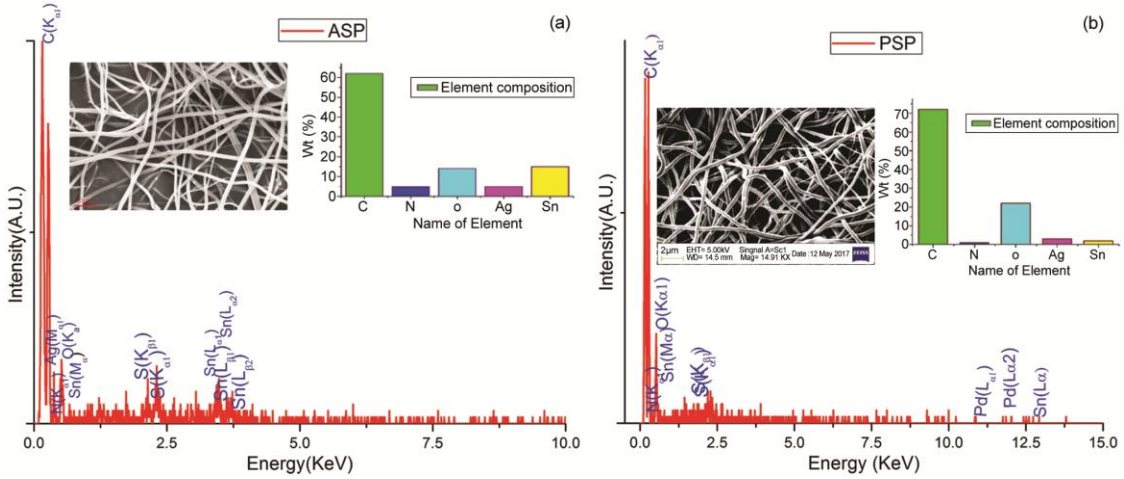

Fig. 3 — (a) EDAX pattern of ASP nanofibers; and (b) EDAX pattern of ASP_1 nanofibers.

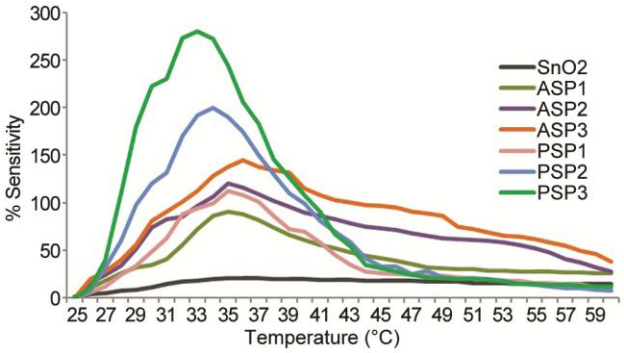

Fig. 4 — Variation of % sensitivity with temperature for hydrogen gas.

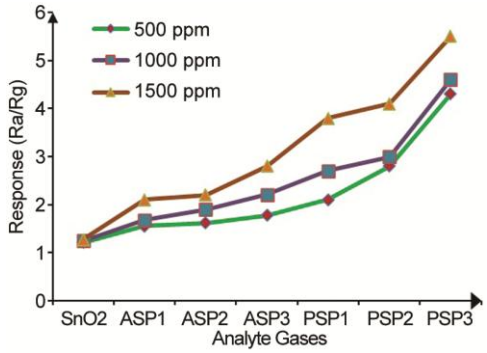

Fig. 5 — Response curve for SnO_2, ASP and PSP nanofibers at different concentration of hydrogen gas.

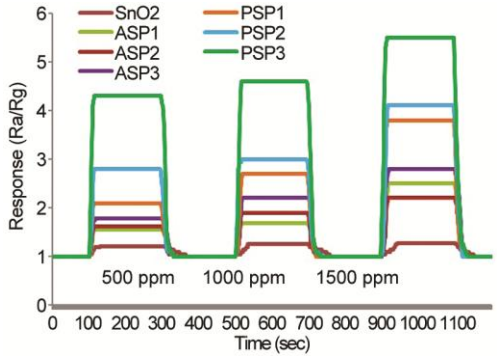

Fig. 6 — Response curve for SnO_2, ASP and PSP nanofibers with time.

atom (Hydride) and releases electron during this process. This effect is known as spill-over effect. It is believed that spill-over effect modifies the response of Pd doped SnO_2 nanofibers.

The proposed model for sensitization of hydrogen interaction with O^- species over Pd decorated SnO_2 surface is described below.

$$H_2\,(\mathrm{g}) \rightarrow 2H_{(Pd)}(\text{Split-over}) \quad \ldots (1)$$

$$4H_{(Pd)} + O^-_{2(SnO\,2)} \rightarrow 2H_g(g) + e^-_{(SnO\,2)}(\text{Spillover}) \quad \ldots (2)$$

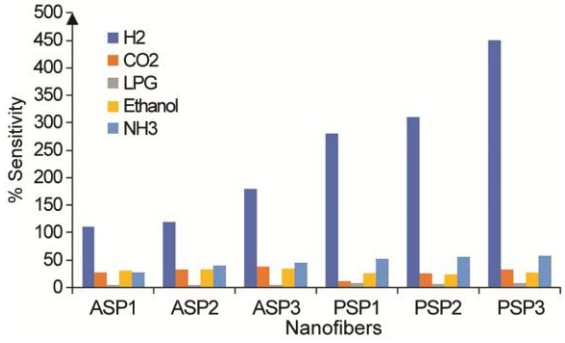

Fig. 7 — Selectivity of Hydrogen and other gases for SnO_2, ASP and PSP nanofibers.

$$2\mathrm{H}_{(\mathrm{Pd})} + O^-_{(SnO)} \rightarrow H_2O_{(g)} + e^-_{(SnO)}(\text{Spillover}) \quad \ldots (3)$$

The chemical sensitization shown in above equations stimulates the response of the sensor towards Hydrogen gas. ASP and PSP nanofibers have been studied for cross selectivity of the Hydrogen gas with other atmospheric gases. Atmospheric gases and vapors such as H_2, CO_2, HCl vapors, Ethanol vapors and NH_3 vapors are allowed to pass over nanofibers. The selectivity of ASP and PSP nonofibers has been studied at 32 ^{0}C temperature for 500 ppm of all analyte gases and vapors. Highest sensitivity is visible for nanofibers in presence of hydrogen as depicted in Fig. 7.

4 Conclusion

ASP and PSP nanofibers are studied for hydrogen gas sensing. The nanofibers are formed by electrospinning method. XRD and SEM study is done for investigation of morphological properties of nanofibers. SEM study reveals that the diameter range of ASP nanofiber and PSP nanofiber is 72-562 nm and 96-620 nm respectively. Surface structure modifications are achieved by dip coating of nanofibers during polymerization which could provide coating of conducting polymers onto semiconducting oxide. The coating of PANI enhances the conductive nature of SnO_2 nanofibers. Higher activity of ASP and PSP is observed owing to synergetic effect of Palladium (Pd) and Silver (Ag) doping to SnO_2 matrix. Improved conductivity of nanofibers not only assisted in lowering the working temperature to the range 30^{o}C-40^{o}C but also improve the response time to 12-18sec.These nanofibers show good sensitivity and selectivity to hydrogen gas near room temperature. Various doping percentage of noble metals can be studied for further refinement of the hydrogen gas sensing. Hydrogen gas sensitivity of ASP and PSP nanofibers can be compared with other

synthesis techniques such as magnetic sputtering, spray pyrolysis and thin films in future work.

Present market uses different materials for commercial hydrogen gas sensor which include electrochemical cell and SMO. PSP nanofibers can be thought as commercial sensor due to its higher response, good sensitivity and selectivity.

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