

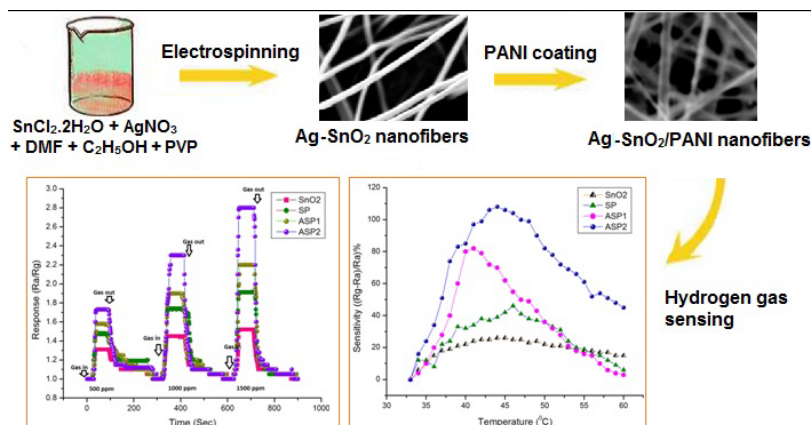
Ag-SnO₂/Polyaniline composite nanofibers for low operating temperature hydrogen gas sensor

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Submitted on: 29-Jan-2017, Accepted on: 22-Mar-2017, Published online: 23-Mar-2017

ABSTRACT



Silver doped tin oxide (Ag-SnO₂) nanofibers were fabricated by electrospinning and subsequently calcinations technique. Ag-SnO₂/polyaniline (PANI) composite nanofibers were prepared by facile in-situ polymerization dip-coating technique. As-synthesized composites nanofibers were characterized by XRD, SEM and studied for hydrogen gas sensing. Ag-SnO₂/PANI composite was found to be more sensitive for hydrogen gas at low operating temperature around 42^oC compared to that of pure or doped SnO₂ nanofibers required more than 250^oC. Further, the response and recovery time of SnO₂/PANI (SP), 1%Ag-SnO₂/PANI (ASP1) and 2%Ag-SnO₂/PANI (ASP2) composites were obtained at different concentrations 500-1500 ppm of hydrogen gas at an operating temperature of 42^oC. The good stability and lowest response as well as recovery time were observed for ASP2 composite for all concentrations of hydrogen gas compared to that of pristine SnO₂ and other composites.

Keywords: Ag doped SnO₂, Polyaniline, Nanofibers, Electrospinning, Composites, Hydrogen gas sensor

INTRODUCTION

Conventional semiconducting metal oxides are widely employed for the gas sensing application due to their ability to

detect traces of the gas of order of few part per billion (ppb).¹ The improved response towards target gas is due to high surface to volume ratio of semiconducting metal oxides. These materials are extensively used for reducing gas detection, e.g. hydrogen, ammonia etc and oxidizing gas like oxygen, ethyl alcohol.^{2,3} It is observed that sensing response to the gas can be controlled with the grain-size of molecules by reducing it to nanosize.⁴ In recent years, there has been significant progress in one-dimensional (1D) nanostructures due to their unique physical and chemical properties. Compared to other three dimensions, 1D nanostructure are highly suitable for moving charges in integrated nanoscale systems due to their low dimension structure and high aspect ratio,

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Cite as: *J. Mat. NanoSci.*, 2017, 4(1), 13-18.

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which could efficiently transport electrical carriers along one controllable direction. They have been demonstrated to be a novel and excellent candidate for the advanced applications, especially for gas sensors. Various techniques, such as template-assisted approach, chemical vapour deposition, hydrothermal method, and electrospinning have been useful for the synthesis of 1D. Among them, electrospinning is an efficient and economical method to generate nanofibers of semiconducting metal oxides. They have been successfully fabricated and widely utilized for gas sensors due to their sensing properties based on the surface reaction between the metal-oxides and adsorbed gas species on exposure to specific gas. Therefore, a number of studies have been reported on the synthesis of doped or composite nanofibers via electrospinning technique for applications of gas sensors. There are numbers of metal oxide semiconductor based gas sensors, such as SnO₂, Fe₂O₃, ZnO, WO₃, TiO₂ and In₂O₃.⁵⁻¹¹ Among the various semiconducting metal oxide, tin oxide SnO₂ is a remarkable n-type semiconductor having wide band gap (~ 3.6 eV) and by making use of small quantity of dopant into its matrix, thin film of this material find use as gas sensors for the detection of H₂, NH₃, CO and NO₂ gases.¹² Nanofibers of pure SnO₂ has been exposed with high sensing characteristics. The efforts have been made to increase the sensitivity of SnO₂ for gas sensing by doping of Nobel metal like Ag, Au, Pt, Pd, Nb, Al and F etc, but the high operating temperature (200-400°C) of these sensors may be inadequate for measuring high gas concentrations due to the danger of explosions of inflammable gases like hydrogen gas.¹³⁻¹⁷ Therefore, much effort has been focused on development of gas sensors with low power consuming at low operating temperatures by new materials.

Conducting polymers are new class of sensing materials, which can be prepared by a simple chemical oxidative polymerization method. They have improved the gas sensing properties especially in lowering the operating temperature to around room temperature. In addition to this, the ability to incorporate specific binding sites into conducting polymers promises an improvement of selectivity and sensitivity of material.¹⁸⁻²² Among all synthesized conducting polymers, polyaniline (PANI) is a typical p-type semiconductor and possessed distinctive redox property, controllable conductivity and good thermal stability. However, PANI is not as sensitive as metal oxides towards gas species and its poor solubility in organic solvents limits its applications. Addition of highly sensitive SnO₂ improves its sensitivity towards the gas species due to synergistic effect.²³ 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/SnO₂ composite had excellent gas sensing properties.

In this paper, we report the fabrication of Ag doped SnO₂/PANI composites nanofibers using electrospinning and dip-coating polymerization techniques for the sensing of hydrogen gas. The result showed quick response, high sensitivity and low working temperature of the sensor. This result depicts efficient use of sensor with low cost and high performance compared to that of pure metal oxide nanofibers.

EXPERIMENTAL

Preparation of Ag-SnO₂/PANI nanofibers

In a typical procedure to fabricate Ag doped SnO₂ fibers, 0.2 gm stannous chloride (SnCl₂.2H₂O) and 0.002 gm (1wt%) silver nitrate (AgNO₃) are dissolved in 2.3 ml dimethyl formamide (DMF) and 2.6 ml ethanol (C₂H₅OH). The solution was magnetically stirred for half an hour. 0.5 gm poly(vinylpyrrolidone) PVP was then added to the solution and stirred for half an hour. PVP is an important parameter for drawing fibers with nanoscale diameter by electrospinning. PVP with high molecular weight and lower melting point than SnO₂ was used to draw bead free nanofibers. The solution was filled in 10ml disposable syringe and loaded for electrospinning at room temperature. The needle of the syringe was electrically connected to a positive high voltage of 18 kV and kept at a distance of 23 cm from stationary collector (aluminum foil).²⁴ The solution flow rate was kept at 0.5 ml per hour, maintained using computer control programmer. Nanofibers were collected from the foil and dried at 80°C for 12 hours. The dried nanofibers were then calcined at 300°C for 4 hour to evaporate PVP and to form Ag-SnO₂ nanofibers. Further, Ag-SnO₂ nanofibers were used for coating polyaniline to form Ag-SnO₂/PANI (ASP1) nanofibers by using dip-coating in-situ chemical oxidative polymerization process. In the typical process of polymerization, 5.5 gm of CSA (camphor sulphonic acid) as dopant was mixed in a solution of 50 ml double distilled water and 0.9 ml aniline. 2.2 gm ammonium peroxydisulphate (APS) as oxidant was dissolved in 50ml double distilled water and mixed to aniline solution drop wise at 5°C while stirring for 5 hours. Ag-SnO₂ nanofibers were inserted into the solution during polymerization using dip-coating technique. Ag-SnO₂/PANI nanofibers were dried at 80°C in vacuum oven. Pure SnO₂ and SnO₂/PANI (SP) nanofibers were also prepared without the use of AgNO₃ for gas sensing comparison purpose. 2wt% Ag doped SnO₂/PANI (ASP2) composite nanofibers were also prepared to compare with ASP1 for gas sensing behavior.

Characterizations

X-ray diffraction (XRD) of as-fabricated electrospun nanofibers was carried on Rigaku D/MAX-RB X-ray diffractometer recorded using Cu-K α radiation with the scan rate 1°/min. The surface morphology was investigated by using scanning electron microscope (Carl Zeiss EVO-18). Hydrogen gas sensing was performed by using a laboratory built setup with computer programming to measure resistance verses temperature and time. Two cylinders of air and hydrogen were used for alternate passage of the air and hydrogen gas into the glass chamber. The gas chamber consists of sample holder, electrode for resistance measurement, heating arrangement with temperature controller as shown in scheme 1.

RESULTS AND DISCUSSION

Figure 1 (a) and (b) shows SEM images of Ag-SnO₂ and Ag-SnO₂/PANI composite nanofibers respectively. SEM images show smooth fibers with several millimeters length and diameter of Ag-SnO₂ fibers was found to be in the range of 400-500 nm. The diameter of Ag-SnO₂/PANI nanofibers was found to be increased

as compared to pristine Ag-SnO₂ nanofibers indicating uniform coating of PANI on the surface of Ag-SnO₂ nanofibers during dip-coating polymerization process. The highly porous structure with high surface area to volume ratio and aspect ratio of as-synthesized nanofibers was found to be suitable nanomaterials for gas sensing as surface is more reactive to absorb the gas molecules.

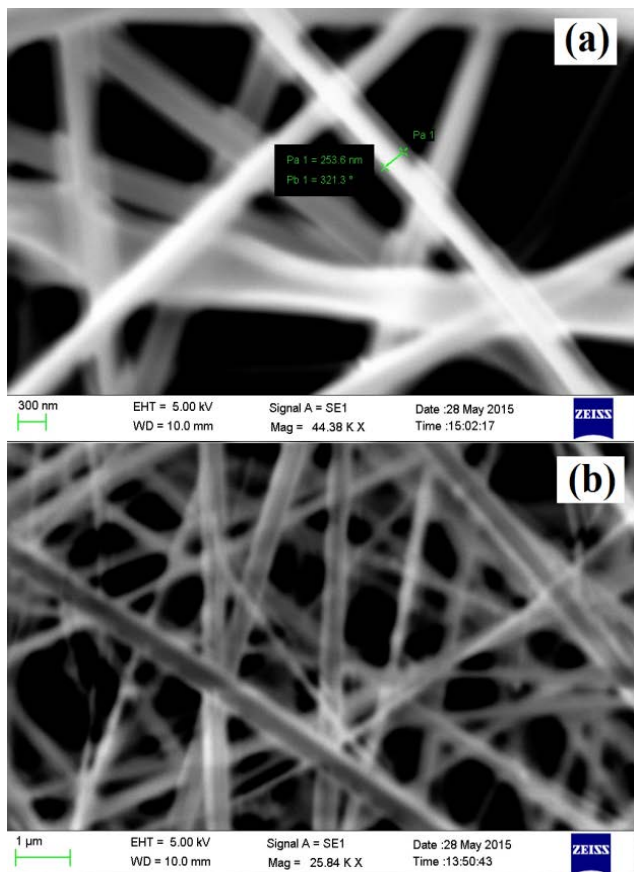
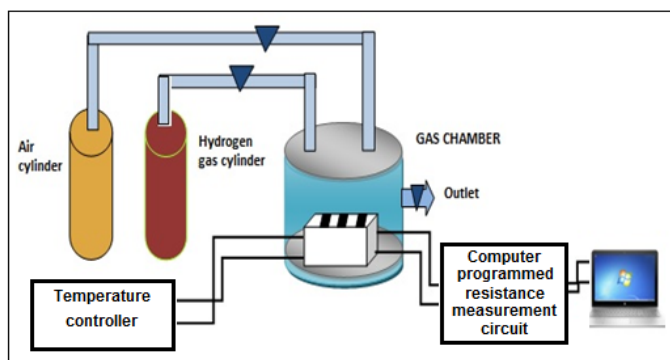


Figure 1: SEM images of (a) Ag-SnO₂ and (b) Ag-SnO₂/PANI composite nanofibers



Scheme 1: Schematic diagram of sensing unit

Figure 2 shows XRD pattern of Ag doped SnO₂, SnO₂/PANI (SP), Ag-SnO₂/PANI (ASP1) and Ag-SnO₂/PANI (ASP2) composite nanofibers. All the strong diffraction peaks of SnO₂ can be perfectly indexed as the tetragonal rutile structure for SnO₂ (ICDD DATA CARD (41-1445)).²⁵ The broadening of the peak

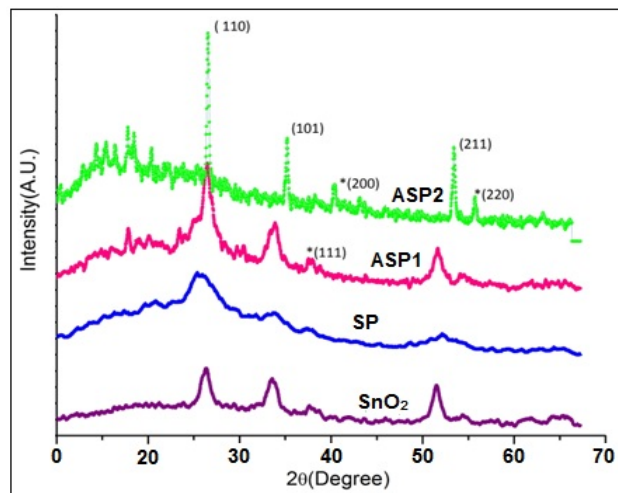


Figure 2: XRD patterns of SnO₂, SnO₂/PANI (SP), 1% Ag-SnO₂/PANI (ASP1) and 2% Ag-SnO₂/PANI (ASP2) nanofibers

pattern is due to the overlapping of PANI and SnO₂ peaks near 26° (JCPDS 41-1445). Strong peaks are identified for SnO₂ at 2θ = 26.6°, 33.8°, 38.2°, 52.4°, 64.6° corresponds to (110), (101), (200), (211), (301). Two strong peaks for Ag are observed at 36.2°, 44.4° corresponding to (111), (200) compared with that of file JCPDS04-0783. The XRD pattern of the polymer generally differs because of uncertainty in the polymeric chains. It depends on the synthetic routes, solvent and ionized state. The prominent peak of polyaniline at 25.4° can be indexed with 110. The broad peak due to PANI around 26° has been found to be merged with that of SnO₂ at 26.66°. The crystallization behaviour of SnO₂ particles was found to be affected by PANI deposition on the surface of SnO₂ particles in the composite. It can be seen that the characteristic diffraction peaks of Ag-SnO₂ are also present in the composites, which proves the existence of Ag-SnO₂ to form hybrid suitable for gas sensing.

As-prepared nanofibers were used for hydrogen gas sensing. In order to test the gas sensing ability of composite nanofibers, the gas sensor unit was specially designed. It consist of two cylinders, one for air and other for H₂ gas connected to the gas chamber using three way stop-cock. Inside the chamber, temperature was maintained with the help of thermocouple (heater controller). There was a glass substrate, on which sample was mounted provided with electrode in order to detect change in resistance of the sample on exposure and de-exposure of hydrogen gas. These electrodes were connected to resistance measuring unit operated via software so that output can be obtained on computer in the form of change in resistance of sensing material with respect to change in time and temperature which shows that electrical resistance is a sensitive parameter in case of sensing. Through the external connections, temperature controlled current-voltage (I-V) characteristic of the conducting nanofibers was recorded. I-V characteristics of the composite nanofibers before and after exposure of gases were recorded for various ppms of gas concentrations. From I-V characteristics, the change in resistance was noted. The electrical resistance of composite nanofibers in air (R_a) and in the presence of gas (R_g) was measured. It is well known that the gas response is greatly influenced by the operating temperature. In order to determine the optimum operating

temperature, the responses of sensors were evaluated by variation in the resistance of the fibers in dry air while heating and cooling the nanofibers. It is clearly observed that the responses of sensors increase firstly with the increase of temperature, and reach their maximum values around 40 °C. Therefore, this temperature was chosen to be an optimized operating temperature for further testing. The hydrogen gas was injected in the gas chamber for recording the change in the resistance. The percentage sensitivity ($\Delta R/R_a$ %) was used as parameter to monitor the sensitivity, where $\Delta R = R_a - R_g$ represents the change in resistance. The higher sensitivity was reported for ASP2 composite nanofibers for hydrogen gas as shown in Figure 3 due to heavily doped of silver (Ag) in SnO₂ and presence of PANI to enhance density of electrons along the chain of PANI providing high reactivity by releasing electron for reduced gas like hydrogen. Thus more sites are available for target gas to react with the Ag-SnO₂/PANI nanofibers. The high sensitivity of the sample was observed at low temperature around 40-45 °C for SP, ASP1 and ASP2 as compared to 300°C for pure SnO₂ nanofibers.²⁵

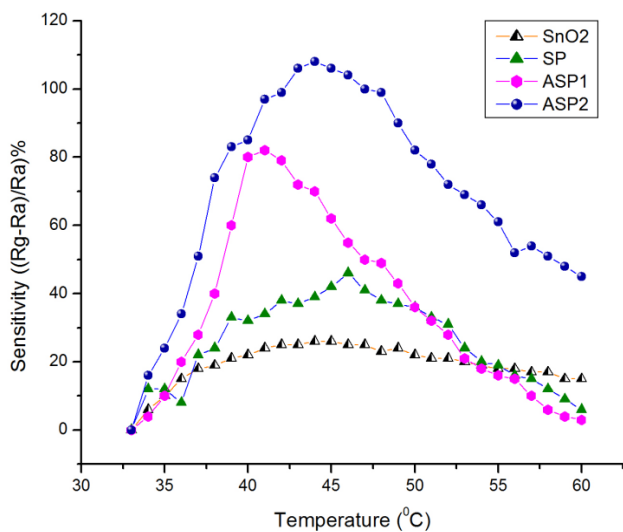


Figure 3: Sensitivity vs temperature for SnO₂, SnO₂/PANI (SP), 1%Ag-SnO₂/PANI (ASP1) and 2%Ag-SnO₂/PANI (ASP2) nanofibers

Response of the sample was accounted using parameter Ra/Rg by injecting dry air followed by hydrogen gas for 500 ppm, 1000 ppm and 1500 ppm. The response of the sample ASP₂ has highest than that of pure SnO₂, SP, ASP1 composites. The response and recovery time of ASP₂ at 40 °C for 1000 ppm of hydrogen gas was found to be 16 sec and 24 sec respectively (figure 4). The response of samples for different concentration at 40 °C shows high response for ASP₂ (figure 5). The stability of nanofibers over the period of 15 days shows that Ag doped SnO₂-PANI nanofibers was found to be more stable than SnO₂ (figure 6). The selectivity of Ag-SnO₂/Polyaniline (ASP₂) has been investigated for different gases like carbon dioxide (CO₂), ammonia (NH₃), LPG, ethanol, etc. The variation of percentage sensitivity for 500, 1000 and 1500ppm at 40°C for different gases is shown in figure 7. The maximum sensitivity is reported for H₂ gas, indicates that Ag-SnO₂/Polyaniline (ASP₂) is highly selective for hydrogen gas.

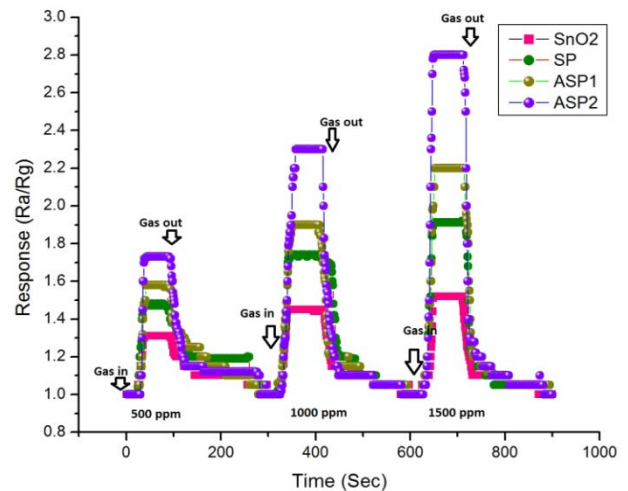


Figure 4: Response and recovery of SnO₂, SnO₂/PANI (SP), 1%Ag-SnO₂/PANI (ASP1) and 2%Ag-SnO₂/PANI (ASP2) nanofibers

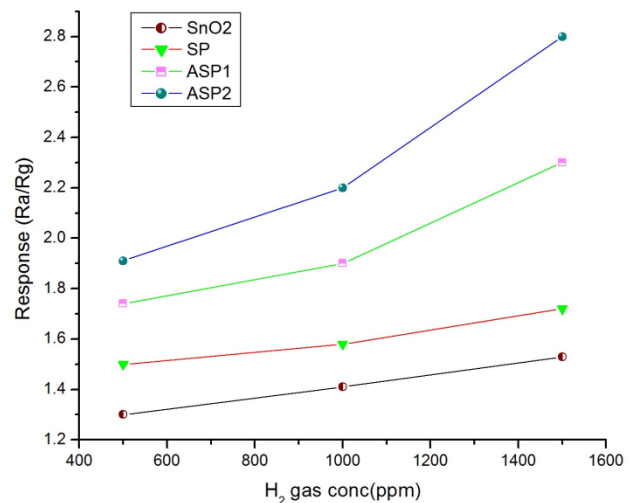


Figure 5: Response vs concentration of hydrogen gas for SnO₂, SnO₂/PANI (SP), 1%Ag-SnO₂/PANI (ASP1) and 2%Ag-SnO₂/PANI (ASP2) nanofibers

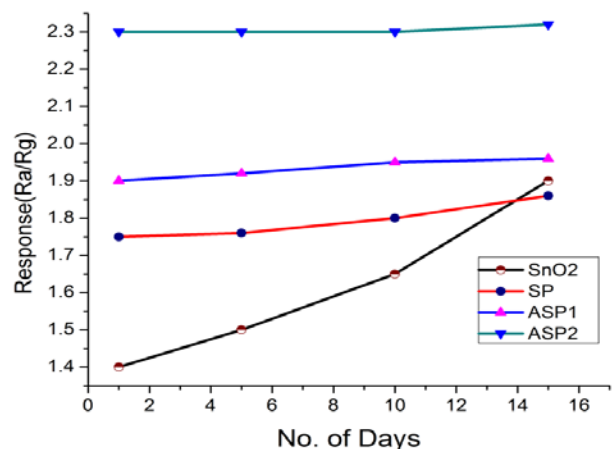


Figure 6: Stability for hydrogen gas sensing of SnO₂, SnO₂/PANI (SP), 1%Ag-SnO₂/PANI (ASP1) and 2%Ag-SnO₂/PANI (ASP2) nanofibers

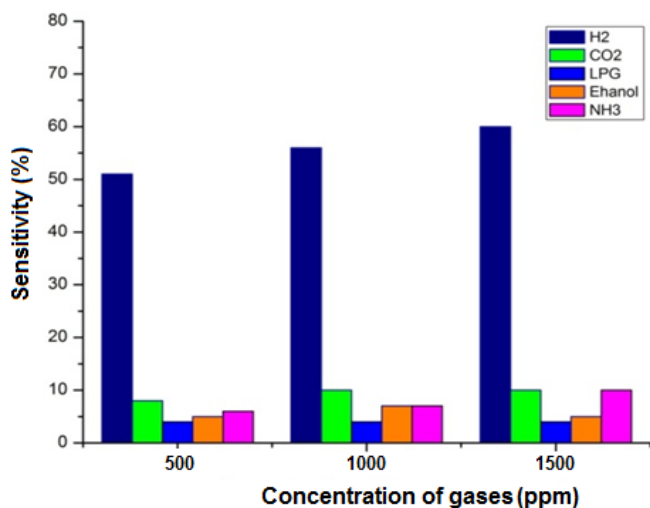


Figure 7: Selectivity of 2% Ag-SnO₂/PANI (ASP2) nanofibers for hydrogen gas sensing

The sensing mechanism of Ag doped SnO₂/PANI nanofibers can be understood by depletion layer form between p-type PANI and n-type Ag-SnO₂. In case of pure SnO₂, when the SnO₂ nanofibers are exposed to air, oxygen molecules are adsorbed on the surface of SnO₂, forming oxygen species such as O₂⁻, O²⁻ and O⁻ by capturing electrons from the conduction band of SnO₂. Consequently, an electron depletion layer is generated on the surface of SnO₂ nanofibers, resulting in an increased sensor resistance. When hydrogen gas is introduced, the molecules of hydrogen react with the adsorbed oxygen species, releasing the captured electrons to the conduction band of SnO₂. Accordingly, the resistance of the sensor decreases due to the increased electron concentration. In case of Ag doped SnO₂/PANI composite nanofibers, it exhibit much higher response values compared to the pure SnO₂ nanofibers. The improvement of hydrogen sensitivity of the composite nanofibers can be ascribed to the formation of p-n heterojunction at the interface between PANI and Ag doped SnO₂ will be generated at the interfaces, resulting in band bending in the depletion layers. During this process, the electrons flow from n-type to p-type while the holes transfer in reverse direction until an equalization of the Fermi levels is achieved. This process results in a much wider electron depletion layer and narrower electrical transport channel.²⁶ The widened electron depletion layer due to the formation of p-n heterojunction contributes greatly to the enhanced gas response properties of Ag doped SnO₂/PANI nanofibers sensor.

CONCLUSIONS

The nanofibers of SnO₂/PANI, 1% Ag-SnO₂/PANI and 2% Ag-SnO₂/PANI composites have been synthesized successfully by electrospinning and dip-coating polymerization. The formation of composite is confirmed by XRD and SEM analysis. The enhanced sensitivity and response of Ag doped SnO₂/PANI composite nanofibers for hydrogen gas sensing was observed at lower temperature between 40-45 °C compared to that of pure SnO₂ nanofibers reported at 300 °C. Further, Ag doped SnO₂/PANI composite nanofibers showed more stability and highly sensitive as well as selective for hydrogen gas sensing.

ACKNOWLEDGMENTS

The authors gratefully acknowledge University Grants Commission, Govt. of India for financial assistance provided through major research project granted to one of the authors to carry out this work.

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