Research Article 2018, **9**(3) 182-187 Advanced Materials Letters

Highly sensitive hydrogen gas sensor based on Al-doped SnO_2/Polyaniline composite nanofibers

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DOI: 10.5185/amlett.2018.1591
www.vbripress.com/aml

Abstract

Metal oxide nanofibers showed keen interest in chemical gas sensing due to their unique chemical and electrical properties at operating temperature more than 200 °C. Their sensitivity can be improved at low operating temperature closed to room temperature by using conducting polymers. In this paper, Al doped tin oxide/polyaniline composite nanofibers detected H_2 molecules at room temperature. A simple versatile electrospinning technique is used for the fabrication of Aluminium (Al) doped (tin oxide) SnO_2 nanofibers and polyaniline was encapsulated using chemical oxidative polymerization (COP) of aniline monomer using ammonium persulfate as redox initiator. The structure and morphology of Al-doped SnO_2/PANI composite nanofibers were investigated by SEM-EDX, UV-VIS and XRD spectroscopy. Structural changes of SnO_2/PANI crystal due to the incorporation of Al^{3+} ions have been explained. Al-doped SnO_2/PANI composite nanofiber is very much selective towards H_2 gas molecules in terms of high sensitivity, rapid response and recovery around room temperature compared to that of Al-doped SnO_2. The present sensing mechanism systematically explained the existence of PN junction which is formed by p-type and n-type semiconductors in Al-doped SnO_2/PANI hybrid composite material. Copyright © 2018 VBRI Press.

Keywords: Al-doped SnO_2 nanofibers; Polyaniline; Composites; p-n heterojunction; Hydrogen gas sensor.

Introduction

Electrospinning is a low-cost, versatile and easy method for the fabrication of one-dimensional (1D) continuous uniform nanofibers. The nanofibers can be prepared by this technique by accelerating high voltage power supply to the solution. When a sufficiently high voltage is applied to the polymer solution, it becomes charged, and due to the electrostatic repulsion, the droplet stretched and erupts from tip of needle. This point of eruption is known as the Taylor cone which finally undergoes an elongation and thinning of fibers deposited onto the collector **[1-2].** 1D structure is a smaller dimentional nanostructure highly suitable for transport of electrons efficiently long one controllable direction. Due to their low dimension, they have high aspect ratio. High surface area and aspect ratio of electrospun nanofibers makes them highly attractive for use as gas sensor as a result of its greater sensing characteristics. Therefore, nanofibers have been developed for sensing various toxic and hazardous gases **[3-5]**. The combination of organic and inorganic materials, conducting polymer composites, and semiconductors formed in the form of nonwoven fiber mats are successfully applied as gas sensing interfaces with the fiber arrangement of single fiber, oriented fibers, or nonwoven membranes at room or elevated operating temperature and their potential applications in optoelectronics, sensors, catalysis, fiber reinforcement, tissue engineering, drug delivery, etc. Polyaniline (PANI) is one of the most important intrinsically conducting polymers due to its advantages of easy synthesis, environmental stability, good chemical stability, high conductivity, and interesting redox properties etc. **[6-10].** However, there is some limitations i.e. poor solubility and low thermal stability due to which pure PANI could not be used for sensing of various gases and also it makes them unsuitable for electrospinning. Generally, the Combination of PANI and metal-oxide or doped metal-oxide such as with SnO_2 or Al-SnO_2 may lead enhanced sensing properties as compared to pure PANI or pure metal oxide due to the synergistic effect of organic and inorganic materials **[11-14].** Many techniques have been developed to enhance their sensing performance such as by the addition of dopants in pure metal oxide or by mixing inorganic in organic material and by the formation of p-n junction. PANI/Al-SnO_2 composite has excellent gas sensing properties compared to that of pure PANI and Al-SnO_2. SnO_2 is an oxygen-deficient n-type semiconductor and its thin films are useful for sensing various hazardous and inflammable gases such as H_2, NH_3, CO and NO_2. But, metal oxide sensing material requires very high operating temperature. . The optimum temperature depends on the material of the fabricated sensor and the kind of gases to detect. The strength of the van der Waals bond between the material and the gas is the most important factor to determine the operating temperature of the sensor. Recently, it has been reported that the addition of uniformly dispersed precious metals like aluminum (Al) nanoparticles on the SnO_2 surface tuned its electrical and optical properties and the interaction between gas and absorbed oxygen on the SnO_2 surface enhanced. Therefore, Al-SnO_2 showed enhanced sensing results than pristine SnO_2. Composite nanofibers of polymers with carbon nanomaterials for the preparation of chemical sensors opens up exciting areas of research due to their biocompatibility, and excellent sensitivity and selectivity **[15, 16].** These composite materials shows high sensitivity, selectivity, reproducibility, robustness, fast response and recovery behavior at low operating temperature due to their synergistic effect **[17-20].** There are more and more toxic gases generated in the environment due to the industrialization. H_2 is widely existed in the air. And H_2 is flammable at concentrations of 4-75% by volume in air. Hydrogen is colorless, odorless and tasteless gas and can leak easily from the gas lines. So H_2 sensors which quickly, reliably and selectively respond to H_2 gas are very much important to save environment. Sensing over large scale can be done easily. But it needs bulky and expensive equipments, which are unsuitable for many other applications.

So we have presented here a hydrogen sensor of the core shell formed by PANI nanostructures i.e. Al-SnO_2/PANI composite nanofibers by chemical oxidative polymerization and electrospinning technique. Sharma et al. **[4]** already worked on individual PANI and composite nanofiber which responded rapidly to 1000 ppm or 0.1% of H_2 gas. Polymers synthesized from in-situ chemical oxidative polymerization technique and coated over metal oxide which act as a substrate can be used as a gas sensor; the aligned metal oxide nanofibers have large adsorption capacity. Aligned Al-SnO_2/PANI fibers prepared by electrospinning and used as a substrate for polymers prepared by dip coating polymerization technique and used them as gas sensor have not presented anywhere in literature. This report shows that, uniform Al-SnO_2 nanofibers were fabricated by an advanced and modified electrospinning, fiber production technique and then PANI nanostructures were grown on the Al-SnO_2 nanofiber surface by in situ solution polymerization. These Al-SnO_2/PANI composite nanofibers between tens of nanometres and several micrometers in diameter showed tunable properties and applications. The uniform composite fibers exhibited selectivity for hydrogen gas at 1000–5000 ppm of gas concentration.

Experimental

Materials / chemicals details

$SnCl_2{\cdot}2H_2O$, Aniline monomer an acidic medium and an oxidant i.e. Ammonium persulfate ($(NH_4)_2S_2O_8$), Aluminium nitrate (Al $(NO_3)_3.9H_2O$, purity 99%), and Polyvinyl pyrrolidone (PVP, Mw=1,300,000) were purchased from Sigma Aldrich. The solution temperature is comprised between 0 and 2 °C in order to limit secondary reactions. In order to prepare polyaniline in the form of the emeraldine salt, polymerization is conducted in an acidic medium ($1 < pH \leq 4$) with the use of various acids or buffer solutions and all other chemicals were of AR grade.

Material synthesis / reactions

The synthesis of Al-SnO_2 nanofibers was briefly given as follows. 0.4 g of $SnCl_2{\cdot}2H_2O$ and 4.4 g of DMF were dissolved in 5ml of ethanol then. 1.0 g PVP and 1% Al $(NO_3)_3.9H_2O$ was mixed into the above solution during stirring. The solution was placed for electrospinning for preparation of nanofibers using high-voltage power supply. The Al-SnO_2 product marked was obtained by calcination in a furnace at 300 °C for 4 h which act as a substrate for composite nanofibers. Al-SnO_2/PANI formed by dip coating of Al-SnO_2 nanofibers by using chemical oxidative polymerization of aniline of 0.2 M. Molar concentration of CSA and APS was 0.5M and 0.2M respectively.

Characterizations / response measurements

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX) were done by Carl Zeiss EVO-18 model SEM-EDX. UV-Visible absorption spectrum was obtained by Shimadzu-UV-1800 spectrophotometer. X-ray diffraction (XRD) pattern was obtained by Philips-PW1710 automatic X-ray diffractometer. A computerized gas sensing system was used to show the resistance variation in synthetic air and in presence of H_2 gas at various temperatures starting from room temperature to measure the operating frequency of the sensors. The sensor was exposed to a hydrogen gas at the sequence of 0.1%, 0.2%, 0.3%, 0.4% and 0.5% concentrations at temperature starting from room temperature. The resistance variation was measured by Keithley 2000 Multimeter. Different concentrations (1000-5000 ppm) of H_2 were obtained by diluting standard H_2 with dry and compressed air. These were obtained from Air Products Limited and had purity levels of 99.99%.

Results and discussion

UV-VIS spectroscopy

UV-Vis spectroscopy was done to investigate the optical properties of synthesized sample **[21].** The UV–Vis spectrum of Al-SnO_2 and Al-SnO_2/PANI composite nanofibers are shown in **Fig. 1**. PANI has two characterization absorption bands at around 338 nm and 628 nm that attributed to π–π^* transition of the benzenoid ring and n–π^* transition of benzenoid to quinoid, respectively **[22].** It has been found that the shapes of UV spectra of nanocomposites are similar to those of PANI and some shift in the bands is observed. Additionally, the peak of Al-SnO_2 around 336 nm where the peak of nanocomposite Al-SnO_2/PANI was around 350 nm which

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shows red shift. In Al-SnO_2/PANI nanocomposites the peak at ~420 nm is based on inter ring charge transfer ratio of benzenoid to quinoid moieties showing n-π^* transition. Furthermore, intensity of the peak around 830 nm in visible region corresponds to π-n transition **[23].** But there is no Al dopant related peak seen here which shows low concentration of dopant related nanoparticles or high dispersion of dopant in the mesoporous SnO_2. This result is in a good agreement with X-ray diffraction patterns of nanocomposite.

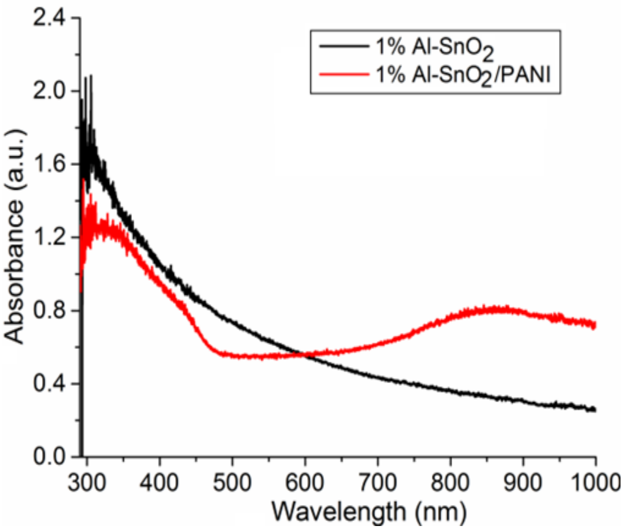

Fig. 1. UV-VIS spectra of nanofibers.

X-Ray Diffraction spectroscopy (XRD)

The crystal structures of the synthesized nanoparticles were investigated by powder X-ray diffraction (XRD). **Fig. 2** shows the XRD pattern of Al-SnO_2 and Al-SnO_2/PANI composite nanofibers **[24].** The XRD spectrum of Al-SnO_2/PANI has a peak at 26.66˚, 34.18˚ and 52.3˚. The characteristic peaks of composite are ascribed to the periodicity in parallel and perpendicular directions of the polymer chain indicate its crystalline as well as its polycrystalline nature. The increase in ordering of composite nanofibers with the addition of Al-SnO_2 indicates that the structure of PANI is strongly influenced by the nanofibers and other strong diffraction peaks of Al-SnO_2 other than composite aroused due to the tetragonal rutile structure for SnO_2 [JCPDS Card No: 41-1445]. The crystal planes (110), (101), (211), (002), (310), (301) were prominently seen in XRD indicating the polycrystalline nature of Al-SnO_2 nanofibers **[25**]. There is no characteristic of Al Diffraction peaks in the pattern was observed which could be due to the low amount of Al doped in the rutile SnO_2 or a homogeneous distribution of Al nanoparticles. It can be seen that the characteristic diffraction peaks of Al-SnO_2 (JCPDS # 77-0451) are also present in the hybrids, which proves the existence of Al-SnO_2 in hybrid, and the crystalline nature of PANI is significantly improved due to more aniline monomer adsorbed on surface of the Al-SnO_2 nanofibers.

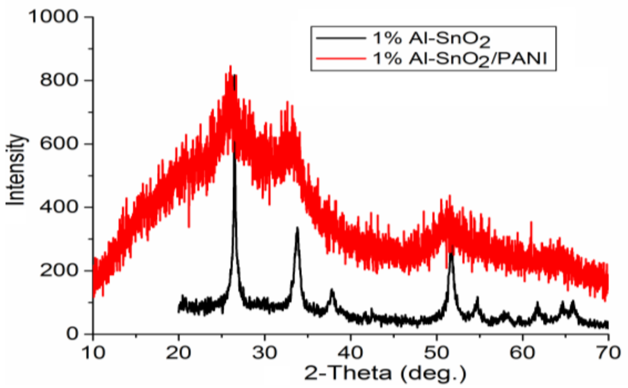

Fig. 2. XRD spectra of nanofibers

Scanning Electron Microscopy (SEM)

The morphology of the nanofibers was investigated by SEM and is shown in **Fig. 3,** after calcinations at 300˚C of Al-SnO_2 nanofibers. During the thermal treatment, PVP was removed. Morphological results show that, homogenous nanofiber with diameters in the range of 150-200 nm was obtained with crystallite sizes were about 10-15 nm. It can be seen that linear nanofibers were covalently cross linked with each other and in composite, the diameter of composite is slightly increased may be due to the encapsulation of PANI over Al-SnO_2 nanofibers. The SEM images showed the presence of smooth, regular and cylindrical morphology of nanofibers. No beads and junctions were observed in the fibers. Al-SnO_2/PANI nanofibers are well organized and aligned than pure Al-SnO_2 and have highly porous structure. It indicates that the composite nanofibers are good for gas sensing.

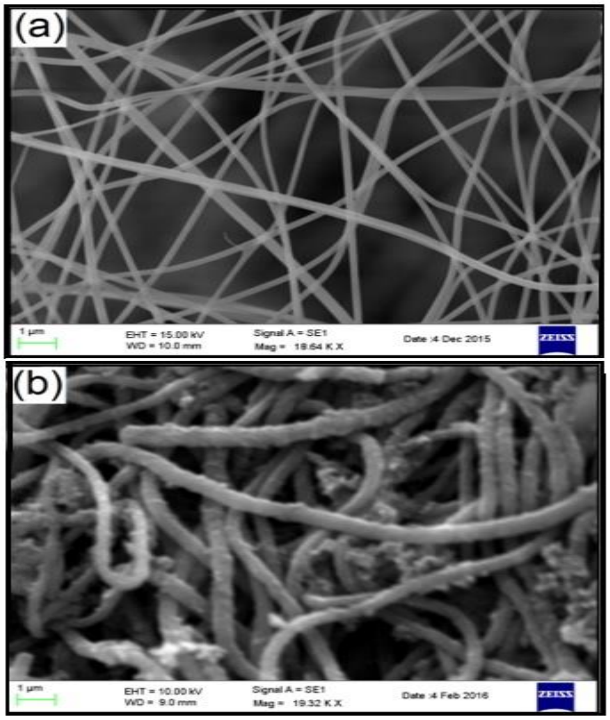

Fig. 3. SEM image (a) Al-SnO_2 and (b) Al- SnO_2/PANI nanofibers.

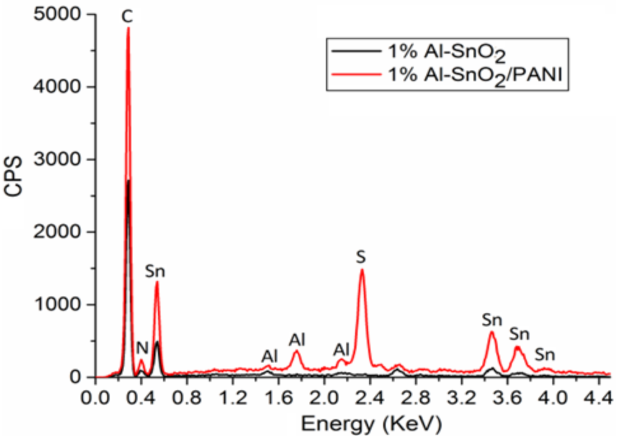

Fig. 4. EDX spectra of (a) Al-SnO_2 and (b) Al-SnO_2/PANI nanofibers.

Energy Dispersive X-Ray Spectroscopy (EDX)

The existence of Al-SnO_2 in PANI was analyzed by energy dispersive X-ray spectrometry (EDX). The EDX spectra of Al-SnO_2 and Al-SnO_2/PANI composite nanofibers are illustrated in **Fig. 4** indicate that the as-prepared nanocomposite is composed of O, Sn, C, Al and N elements. SEM and XRD image confirmed their polycrystalline nature. The Energy Dispersive X-Ray Spectroscopy (EDX) analysis also confirmed that the composite sample consists of a band attributed to sulfur (sKa 2.21 keV) which indicates the incorporation of $–SO_3^-$ as counter ion in the structure of PANI nanofibers. The H signal in composite is not present due to its lower energy. Moreover, EDX analysis was done to prove the incorporation of the doping acids as counter ions in the composite PANI nanofibers. The spectrum shows four characteristic peaks of Sn elements which are presumably due to the x-ray aroused various energy levels in Sn.

Hydrogen Gas Sensing

H_2 has a wide explosive concentration range (4–75vol %), low ignition energy (0.02 mJ) and large flame propagation velocity. Moreover, human senses cannot detect H_2 because it is colorless and odorless. Thus, the ability to accurately detect and monitor hydrogen is important for the safety of environment. Since the concentration of electrons on the surface of metal oxide increases and the resistance of n-type metal oxide layer decreases upon reaction with reducing gas. Al-SnO_2/PANI composite nanofibers sensor showed the diffusion of hydrogen molecules by the depletion layer between metal oxide and polymer due to the formation of heterojunction and the reaction with PANI doped by CSA. Resistance variation of the synthesized composite nanofibers was measured at different hydrogen gas concentrations **[26-27]. Fig. 5** shows the temperature-sensitivity graph of 1% Al-SnO_2/PANI at 1000, 2000, 3000, 4000 and 5000 ppm of hydrogen gas respectively, which indicates the response towards a particular sensing material and indicates an optimum operating temperature. The sensitivity factor (S.F.) of the sensor is defined and expressed as:

$$\text{Sensitivity Factor} = \frac{R_0 - R_g}{R_g} * 100$$

Where, R_0 and R_g are resistance in pure air and Rg is the resistance under a reducing gas such as H_2 **[28-30].**

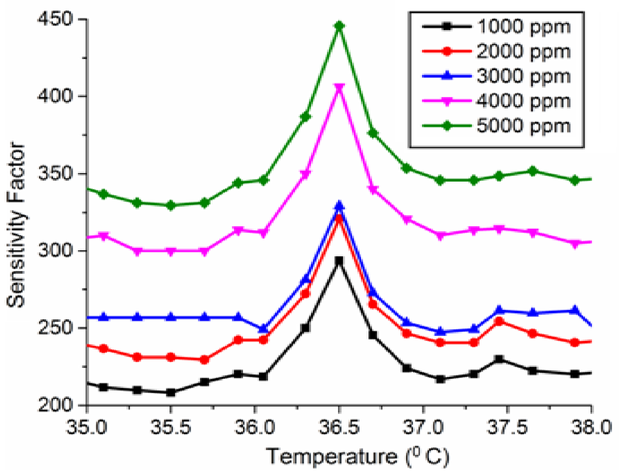

Fig. 5. Sensitivity of Al-SnO_2/PANI composite nanofibers.

The response of the sensor to H_2 gas molecules is shown in **Fig. 6**. The three reversible cycles of the response curve indicated the stable and repeatable characteristics of sensor, as shown in the inset of **Fig. 7** at 36.5˚C for 5000 ppm of H_2 which is the optimum operating temperature of the sensor.

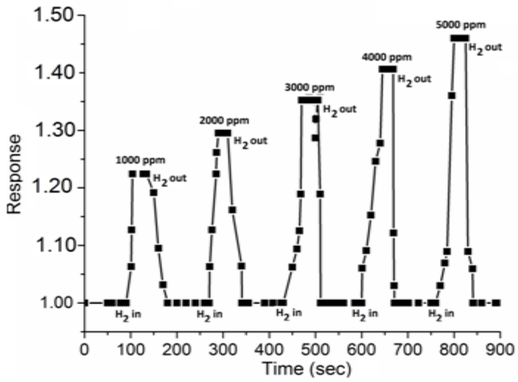

Fig. 6. Response - Time graph of Al-SnO_2/PANI composite nanofibers.

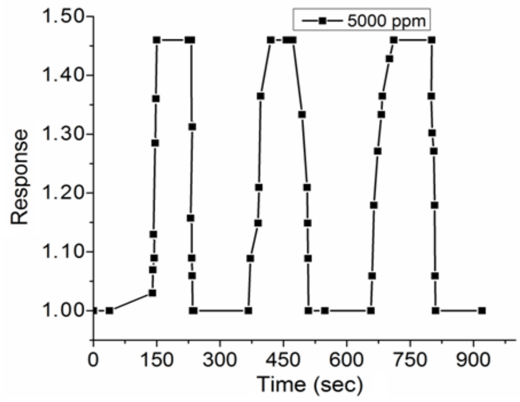

Fig.7. Repeatability of Al-SnO_2/PANI composite nanofibers at 5000 ppm of H_2 gas.

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It indicated that the sensor fabricated in our work exhibited good gas-sensing performances. Response (R_g/R_o) is 1.23 at H_2 concentration at 1000 ppm. During exposure to H_2 for 10 s, the sensitivity is about 290 at 36.5˚C which is working at low temperature compared with the Al-SnO_2 nanofibers sensors reported earlier. And with the concentration increasing to 2000, 3000, 4000 and 5000 ppm, the sensitivity factor is 320, 330, 410 and 440 resp. It is concluded that, as the concentration increases, large quantity of hydrogen molecules will diffuses into the depletion layer. The gas sensing mechanism of sensor is governed by the reaction between the surface layers of the sensor and H_2 gas molecules. **Fig. 6** shows the response-time graph of the synthesized composite sensor at varies gas concentration. Subsequently, the charge transport within the polymer chain returns it to its polaron lattice state with a redistribution of polaron density in the forbidden energy gap that causing new charge transport features create.The increase of the number of carriers and charge transfer rate in the presence of H_2 molecules could cause fully reversible carrier transport (carrier hopping) would be faster in PANI chain.

The mechanism of SnO_2/PANI with hydrogen is based on the formation of heterojunction. For any reducing gas, n-type SnO_2 nanoparticles, increasing its conductivity on interaction thereby decrease the resistance. The adsorbed oxygen molecules on the surface of SnO_2 having O^{2-} O^- and O^{2-} ions which create a positive charge by extracting electrons from their conduction band. This depletion region with the potential barrier of the grain boundaries and/or the necks creates a height basic potential barrier which it hampers the carrier transport in the grains region. When synthesized nanofibers suspend in aniline solution along with APS, the aniline monomers transform to the anilinium cations and an electrostatic interaction between them and adsorbed anions on the surface of nanofibers substrate could be create. The trapped electrons released after interaction, it could create the enhanced carrier mobility. Al is working as a catalyst only thereby increasing the hopping conductivity of the sample. Mechanism is shown in **Fig. 8**. It was found that the Al-SnO_2/PANI composite nanofiber based sensor produce repeatable responses of the same magnitude with good baseline stability. Since the conductivity of SnO_2 is very low at room temperature, the conductivity of the Al-SnO_2/PANI is determined by the PANI coating. The establishment of the p/n heterojunction at the interface of the nanocomposite results in greater resistance change of the nanocomposite towards H_2 than pure PANI in the absence of SnO_2. Literature suggested that, most gas sensors based on one dimensional nanosized SnO_2 or Al-SnO_2 have to be operated at an elevated temperature in order to exhibit their sensing behavior, which is significantly inconvenient for practical applications **[31-33].**

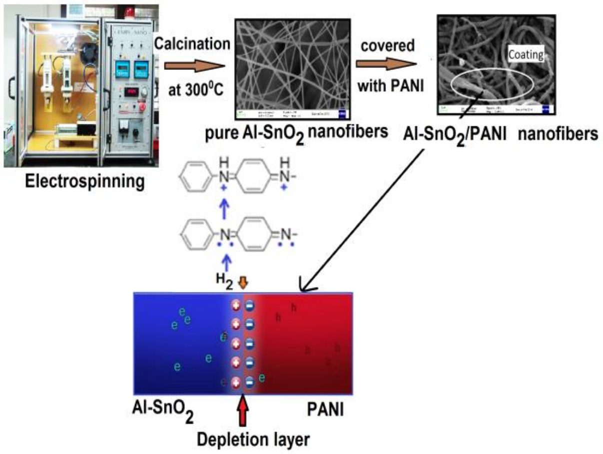

Fig. 8. Mechanism of Hydrogen gas sensing of composite nanofibers.

There are a huge number of p/n heterojunctions in the nanocomposites of Al-SnO_2 nanosheets and PANI, thus the resistance change upon exposure to H_2 is greatly increased, leading to much enhanced response magnitude. In accordance with the proposed model, the establishment of p/n junction plays a crucial role in the comprehensive response of the composite sensor of Al-SnO_2/PANI to H_2, which is in agreement with the observation of higher response magnitude of Al-SnO_2/PANI than the SnO_2/PANI alone.

Conclusion

Al-SnO_2/PANI composite nanofibers based sensor was successfully fabricated with very short response and recovery time, and good reversibility, reproducibility, and stability based on various sensing techniques and PANI was covered over Al-SnO_2 by chemical oxidative polymerization technique. Al-SnO_2/PANI composite nanofibers showed good sensitivity to H_2 gas at 1000 ppm and as the concentration of H_2 gas increases then sensitivity increases rapidly and maximum sensitivity was observed at 36.5˚C for H_2 gas. The sensing mechanism was related to the p-n junction stabilized between p-type PANI and pn-type Al-SnO_2. As-prepared 1% Al-SnO_2/PANI composite nanofibers proved to be an excellent candidate to further increase the sensor sensitivity. It opens a new way to fabricate the ultrasensitive sensors.

Acknowledgements

Authors acknowledge Department of Science & Technology, New Delhi (India) for financial assistance under DST/INSPIRE Fellowship/2013/92, Registration No: [IF130149].

Author’s contributions

Conceived the plan: SBK, HJS; Performed the expeirments: HJS; Data analysis: HJS, SBK, BMB; Wrote the paper: HJS, SBK. Authors have no competing financial interests.

Supporting information

Supporting informations are available from VBRI Press.

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