Synthesis and Characterization of Conducting Polyaniline/Al-Doped Tin Oxide Composite Nanofibers

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Abstract: In this paper, Al-doped SnO_2/PANI composites nanofibers based gas sensors for hydrogen gas sensing application by electrospinning technique and subsequent calcinations are presented. Composite nanofibers have been characterized by X-Ray Diffraction (XRD), Ultraviolet Visible (UV-Vis) spectroscopy, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX). It was suggested that, composite nanofibers showed high sensitivity with relatively faster response/recovery behaviour at room temperature compared to pure SnO_2 and Al-doped SnO_2 nanofibers reported earlier.

Keywords: Nanofibers; aluminium doped tin dioxide; polyaniline; electrospinning; hydrogen sensing.

1. Introduction

In air-quality control, hydrogen gas sensor is very important as hydrogen gas is colorless, odourless, and extremely flammable gas due to which there have been significant efforts to enhance the sensitivity of hydrogen gas sensors to be operated at low temperature. To ensure the safety of hydrogen, efficient and safety hydrogen sensors are still demanded [1]. In recent years, there has been significant progress in one-dimensional (1D) nanostructures due to their unique physical and chemical properties. Compared to the 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, which could efficiently transport electrical carriers along one controllable direction [2, 3]. Nanofibers can be identified as 1D fibers having diameters between tens and hundreds of nanometres. This nanoscale diameter of fibers can give an enormous surface area per unit mass [4, 5]. Nanofibers of Al doped SnO_2 have been exposed with high sensing characteristics, 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 [6-10]. Polyaniline (PANI) has been investigated as a potential material for gas sensing applications, due to its controllable electrical conductivity, environmental stability and interesting redox chemistry (or electroactivity), especially to lowering the operating temperature to around room temperature [11]. So, hybridization of doped metal oxide and conducting polymer could improve the properties of metal oxide or conducting polymers gas sensor and the new synthesized material shows the synergistic effect of these two materials. However, hydrogen is colorless, odourless, and extremely flammable gas with lower explosive limit of 4% in air [12]. Thus, to meet the requirements, there have been significant

efforts to enhance the sensitivity of hydrogen sensors. To ensure the safety of hydrogen, efficient and safety hydrogen sensors are still demanded [13].

2. Experimental

2.1. Materials and methods: Tin chloride ($SnCl_2 \cdot 2H_2O$, purity 99%), Aluminium nitrate (Al $(NO_3)_3.9H_2O$, purity 99%), aniline (purity 98.5%), ammonium peroxydisulphate (APS, purity 99%), Camphor sulfonic acid (CSA, purity 99%) and polyvinyl pyrrolidone (PVP, Mw=1,300,000, purity 99%) were purchased from Sigma-Aldrich. Aniline was purified under reduced pressure prior to use for synthesis. All other chemicals were used as received without any further purification.

Scanning electron microscopy was done by using SEM model - Carl Zeiss EVO-18. UV-Visible absorption spectra were recorded on Shimadzu UV-1800 spectrophotometer. X-ray diffraction patterns were obtained on Philips PW1710 automatic X-ray diffractometer. The gas sensing behaviour was studied by using laboratory built up sensing apparatus by measuring change in the resistance of sensing film with temperature towards pure air and hydrogen gas exposure. The resistance variation was measured by Keithley 2000 Multimeter and temperature was controlled by Temperature Controlled VI Characterization System.

2.2. Preparation of Al-doped SnO_2 nanoparticles and Al-doped SnO_2/PANI composite nanofibers: Sol-gel method was used for the synthesis of Al doped SnO_2 nanoparticles. In a typical method, 0.1M $SnCl_2 \cdot 2H_2O$ and 1 wt% Al $(NO_3)_3.9H_2O$ was added in 1M starch solution and the mixture was stirred for half an hour. Then 0.2M ammonia was added drop wise in the solution under constant stirring. The stirring was continued for further 2 hours and then the solution was allowed to settle for overnight. Supernatant liquid was then discarded carefully and the remaining solution was centrifuged for 10 minute and then filtered. The precipitate of SnO_2 was washed completely using double distilled water to remove by-product and the excessive starch those were bound with the nanoparticles. The product was dried at 80°C for overnight. Then powder was sintered at 600°C for 6 hours and nanocrystalline SnO_2 was obtained.

For the preparation of Al-SnO_2/PANI composite nanofibers, 0.4 g of as-synthesized Al- doped SnO_2 nanoparticles and 0.4 g of CSA doped PANI as-prepared from chemical oxidative polymerization, were dissolved in 10 ml DMF under vigorous stirring for 30 min at room temperature and the solution was ultrasonicated for 15 min. Subsequently, 1.0 g of PVP was added and stirred for further 45 min so as to form a desired viscous solution. Then the solution was loaded into a glass syringe having a stainless steel needle of an orifice of 0.5 mm and electrospun by using ESPIN-NANO modified electrospinning at an applied electric field of 17 kV and flow rate of 0.4 ml/hr. Nanofibers were collected on aluminum foil wrapped on rotating collector which was grounded and fixed at a distance of 20 cm from needle. Nanofibers collected on foil were dried to remove the organic constituents of PVP.

3. Results and discussion

3.1 Scanning electron microscopy: SEM images of Al-doped SnO_2/PANI composite nanofibers are shown in Fig. 1 respectively. From SEM micrographs, the average diameter of as-synthesized Al-doped SnO_2/PANI composite nanofibers were found to be less than 500 nm.

3.2 Energy Dispersive X-ray (EDX) Spectroscopy: EDX has been used to investigate the compositions of the sample, and the spectra are illustrated in Fig. 2. From the EDX pattern, the Al peak can be detected confirming the existence of Al component in the sample.

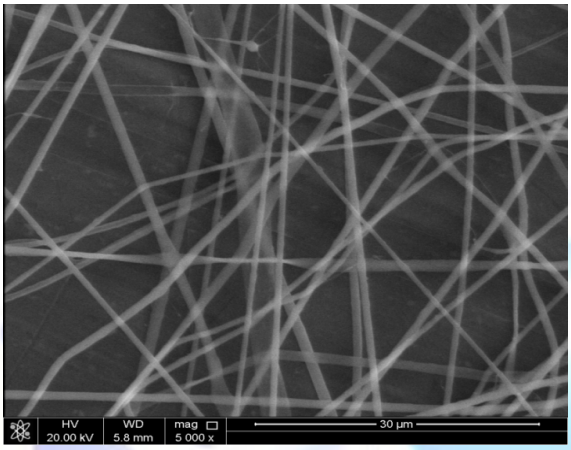

Fig. 1: SEM image of Al-SnO_2/ nanofibers

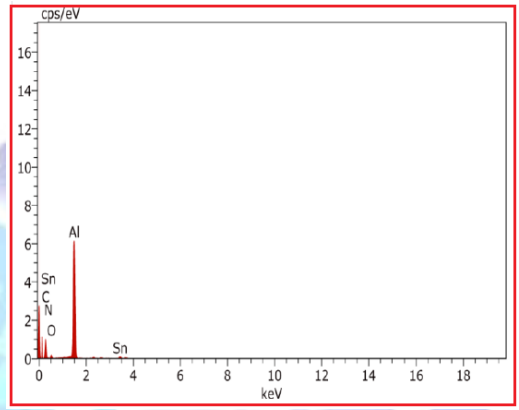

Fig. 2: EDX spectra of Al- PANI SnO_2/PANI nanofibers

3.2 UV-VIS Spectroscopy: UV-VIS spectra of Al-doped SnO_2/PANI composite nanofibers are shown in Fig. 3. Composite nanofibers showed two characteristic bands as compared to a band only in UV region for Al-doped SnO_2. The band in Al doped SnO_2/PANI at 404 nm in visible region corresponding to inter ring charge transfer ratio of benzenoid to quinoid moieties showing polaron-π*. The band at 324 nm in UV region corresponding to π-π* transition of benzenoid [14-16].

3.3 *X-Ray Diffraction :* Fig.4 shows the XRD patterns for 1% Al-SnO_2 and 1% Al-SnO_2/PANI nanofibers. All the strong diffraction peaks of Al-SnO_2 nanofibers can be perfectly indexed as the tetragonal rutile structure for SnO_2 (ICDD DATA CARD 41-1445), Chang et al. (2008). There is no indication of the presence of any dopants-related diffraction peaks for the Al-doped sample implying the high dispersion or the poor crystallinity of dopant related nanoparticles. In the Al-SnO_2/PANI nanofibers, most of the peaks are found to be broadened due the polycrystalline effect of PANI as compared to those of Al-SnO_2. PANI deposited on the surface of Al-SnO_2 particles has no effect on the crystallization behaviour of Al-SnO_2 particles in the nanocomposites.

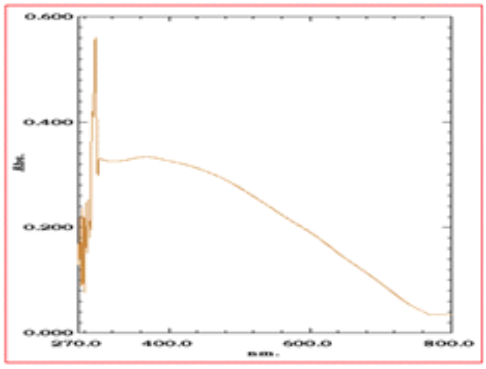

Fig. 3: UV-VIS spectroscopy of PANI/Al-SnO_2 nanofibers

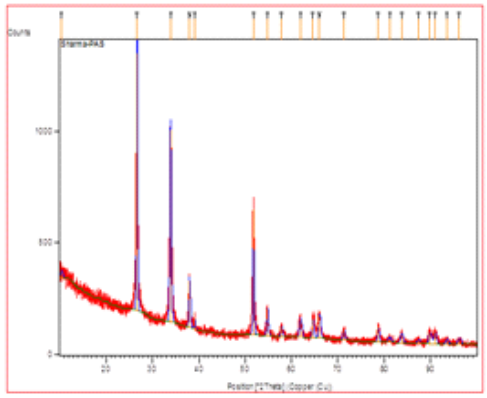

Fig. 4: XRD patterns of Al-SnO2/PANI

3.4 Hydrogen gas sensing: In order to systematically investigate the gas sensing properties of Al-doped SnO_2/PANI composite nanofibers, the study of gas sensing response with time and sensitivity with temperature was carried out towards 1000 ppm of H_2 gas. The sensitivity of Al-doped SnO_2/PANI composite nanofibers to 1000 ppm of H_2 gas at different temperature is shown in Fig. 5. The sensitivity of Al-doped SnO_2/PANI composite nanofibers was found to be increased and reached its maximum around 48 °C for 1000 ppm of H_2 gas. The response of sensor was monitored in terms of the normalized resistance calculated by Response = R_o/R_g and the sensitivity factor was monitored in terms of the % sensitivity calculated by % sensitivity = $\Delta R/R_o$. Where, ΔR is the variation in resistance of composite films from baseline after exposure to H_2 gas, R_g is the resistance of the sensor in presence of H_2 gas and R_o is the initial baseline resistance of the sensor. The suitability of composite nanofibers as H_2 gas sensor was also investigated in terms of 'Response time (R_P)' and 'Recovery time (R_C)'. The response of the composite nanofibers was observed with respect to time of expose to hydrogen gas and air as shown in Fig. 6. The values of R_P and R_C were found to be ~2 sec and ~2 sec for Al-doped SnO_2/PANI.

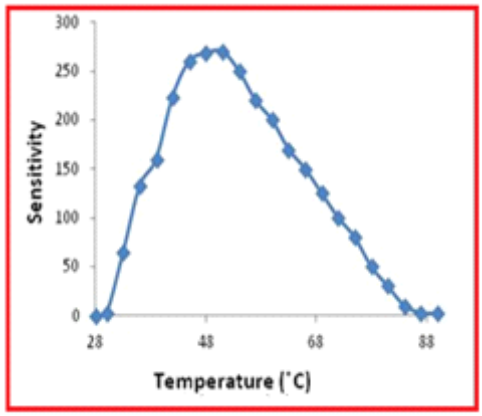

Fig. 5: Sensitivity of Al-doped SnO_2 /PANI composite nanofibers

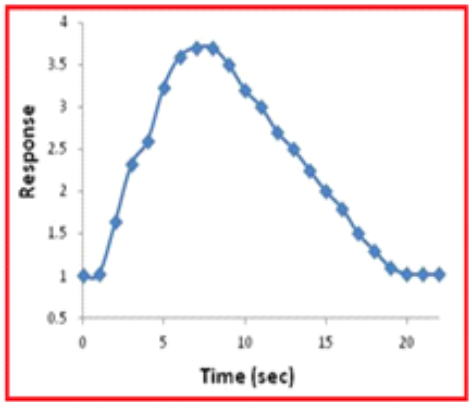

Fig. 6: Response of Al-doped SnO_2 /PANI composite

4. Conclusion

The nanofibers of Al-SnO_2/PANI composite with the diameter around 200-300 nm were synthesized successfully via electrospinning technique. The interaction between aluminum doped SnO_2 and PANI was confirmed from UV-VIS and XRD spectra. It is expected that, in comparison to the pure SnO_2, Al-SnO_2 and PANI based sensors reported earlier; the 1% Al-SnO_2/PANI sensor in the present study exhibits the faster response and higher sensitivity for hydrogen gas at room temperature.

Acknowledgement

The authors acknowledge Department of Science & Technology, New Delhi (India) for financial assistance under; INSPIRE Fellowship 2013. Sanction Order No. & Date: DST/INSPIRE Fellowship/2013/92, dated 17th May 2013. Registration No: [IF130149].

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