FABRICATION AND APPLICATIONS OF (SnO2-ZnO)/POLYPYRROLE(PPy) COAXIAL NANOCABLES TO RESPONSE NH3 GAS

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ABSTRACT

In the study, the purification of andrographolide from Andrographis paniculata was carried out using various physical separation methods such as extraction and crystallization followed by drying. Extraction of andrographolide was carried out using various solvent. The ratio of the solvents was checked for extraction efficiency. The ratio of andrographolide / solvent was found to be 1: 3. 5 weight / volume offers a higher degree of purity of andrographolide. A solubility study of andrographolide was investigated. The extract obtained after the extraction was then treated with activated charcoal in order to remove undesired impurities that could disrupt the crystallization process. The extract was concentrated by evaporation after clarification. The cooling crystallization process was effectively used to further purify andrographolide to obtain 95% high purity andrographolide. The crystallization process was examined from the point of view of supersaturation (more purified output). Andrographolide was confirmed by Thin Layer Chromatography, Melting point, Infra-Red, NMR and Mass Spectra. To look for the morphology of purified andrographolide inverted microscopy and SEM was used. It has been observed that Andrographolide gives different sizes of whitish cuboid crystals of the order of 30µ m- 40 µm.

Keywords: *Crystallization, herbal products, medicinal plant, anti-pyretic.*

I. Introduction

Day by day, the environment is being uncomfortable for breathing due to the many dangerous gasses present in the atmosphere. Therefore, it is vital to detect such harmful gases in order to control air pollution, prevent human life, and protect nature from being damaged. Many people are facing problems with toxic, combustible and volatile gases in the atmosphere including domestic, laboratorial, and industrial places. One such hazardous and toxic gas is ammonia and hence its detection is very important task. This gas, in general is used in many places and in many applications, such as for cooling purposes in the industries [1-3] and medical diagnoses [4-6]. Thus, many researchers are developing affordable and reliable techniques and methods for the detection of ammonia as well as other toxic gases [7-8].

Conducting polymer ammonia gas sensors, at room temperature (300 K) have shown better detection responses among the various material used sensors which work at high temperatures [9]. At low temperature, sensor life will be more and power consumption is less which makes easer operation of the sensor [10-15]. Many notable features, such as low energy optical transitions, controllable electrical conductivity, low ionization potential, and high electron affinity have been shown by conducting polymers, which can be synthesized either by electro-chemical or polymerization of pyrrole (Py) monomer [16-20]. Polypyrrole (PPy), being most stable conducting polymer under ambient conditions has attracted attentions in sensing NH3 gas due to its unique conducto-metric response to ammonia [21-23]. When surface to volume ratio is higher, more potential places are there for reactions to occur then this causes the best and more accurate sensing mechanism of PPy as chemical reactions which take place on the surface.

In the present work, (SnO2–ZnO)/PPy nanocables had been synthesized via electro-spinning method and vapor-phase polymerization of Py on the surface of SnO2–ZnO nanofibers. The core–sheath structure of prepared nanocables was confirmed by Transmission electron microscopy (TEM). The fabricated sensor could detect ammonia gas with fast response and recovery time. It also manifested linear response to ammonia concentration. The determination of NH3 gas concentration becomes more feasible due to linear behavior of graph.

II. Experimental

A. Synthesis of (SnO2 -ZnO)/PPy nanocables

To synthesize SnO_2-ZnO composite nanofibers, 2g polyvinyl alcohol (PVA) was dissolved in 18 ml distilled water, followed by adding 1g Zinc Acetate and 1g Stannous Chloride to prepare electrospinning solution. This mixture was kept at 60^0C for 4h under constant stirring at 400 rpm speed. The electrospinning process was performed with a constant feeding rate of 0.3 ml/h and 8 cm distance between the tip of the syringe and the Al plate collector while the 16 kV electric potential was maintained. The calcination of electrospun nanofibers was done in the furnace at 700^0C for 3 h which resulted in the formation of SnO_2-ZnO composite nanofibers.

On the template of SnO_2-ZnO composite nanofibers, Py monomers in a vapor-phase were polymerized. The soaked template of nanofibers in 0.1 molarity ethanolic $FeCl_3$ solution for 30 min was left in the air for 15 min. This nanofibers template, for about 3h was exposed to saturated Py vapor, due to which, iron (III) ions absorbed on the surface of the nanofibers. Py monomer was oxidized by an iron (III) ion (a). Py dimer and two hydrogen ions will be liberated by bonding two of oxidized Py monomers together (b). By reaction (c), Py dimer will be oxidized using an iron (III) ion and finally a Py trimer resulted by bonding with another oxidized Py (d). This oxidation reaction (e) is given below:

$$Py + Fe^{3+} \rightarrow Py^{+} + Fe^{2+} \quad \text{(a)}$$

$$2Py^{+} \rightarrow Py\text{-}Py + 2H^{+} \quad \text{(b)}$$

$$Py\text{-}Py + Fe^{3+} \rightarrow Py\text{-}Py^{+} + Fe^{2+} \quad \text{(c)}$$

$$Py\text{-}Py^{+} + Py^{+} \rightarrow Py\text{-}Py\text{-}Py + 2H^{+} \quad \text{(d)}$$

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$$Py\text{-}...\text{-}Py + Py^{+} + Py^{+} \rightarrow Py\text{-}...\,Py\text{-}Py + 2H^{+}... \quad \text{(e)}$$

The template was kept hanging up from the vessel containing Py placed on a stirrer which was used for polymerization of Py. For a time about 4 h, Py was heated through stirring. The slow production of black colored precipitates on the template confirmed the PPy formation.

B. Preparation of (SnO2 -ZnO)/PPy nanocables Sensor and its measurements:

On 10 mm x 5 mm x 1 mm alumina substrate, nanofibers were electrospun by electro-spinning procedure. SnO_2-ZnO nanofibers layer was resulted after electrospun nanofibers calcination at 700^0C for 3h. Finally PPy layer was developed on SnO_2-ZnO nanofibers layer. In this way, (SnO_2-ZnO)/PPy nanofibers sensor was fabricated.

By the silver paste, thin Pt wires were cemented to the sample area with a gap of about 1mm [24]. The sample was mounted on thick walled borosilicate glass tubing to form sensor probes. The sensing response of (SnO_2-ZnO)/PPy were recorded at 300 K temperature (Room Temperature) by using two insulated cables connected to the impedance measurement device. 15 ppm to 90 ppm range ammonia gas concentrations were used for the measurement.

Sensitivity is defined as the ratio of resistance of the sensor due to presence of gas to the resistance in air environment and is given by

$$S = \frac{\text{Resistance in presence of gas}}{\text{Original resistance in air}} = \frac{R_{gas}}{R_{air}}$$

Where,

R_{gas} = Resistance of the sensor in presence of NH_3 gas environment and

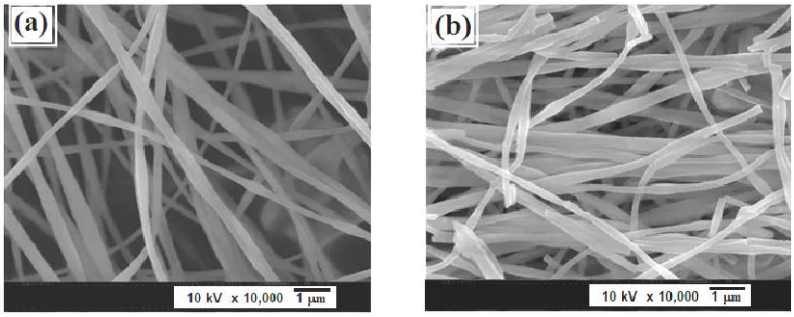
R_{air} = Resistance of the sensor in presence of air.

For achieving 90 % of total resistance change, the time taken by the sensor is known as the response time in case of absorption and in case of desorption, this time is referred as recovery time.

III. Results and Discussions

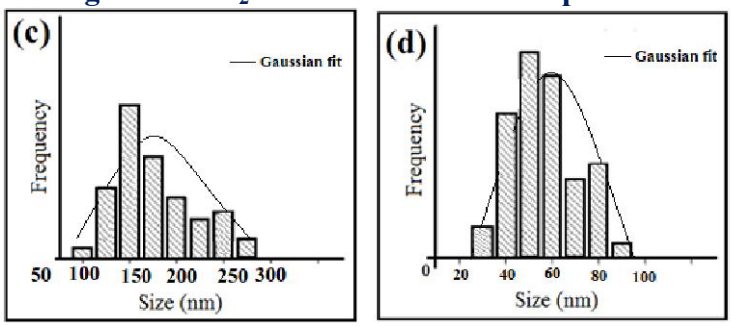
A. Characterization study

The nano-scale dimensions of the fibers and its porosity provided higher accessible surface region, because of which, higher rate of reaction initiated by the diffusion of ammonia gas. The SEM pictures are shown below:



(a) Before calcination (b) After calcination

Figure 1 SnO_2-ZnO nanofibers SEM pictures



(c) Before calcination (d) After calcination

Figure 2 SnO_2-ZnO nanofibers SEM pictures

From figure (1) (a) & (b), it is exhibited that, due the removal of volatile species, diameter sizes of nanofibers reduced. As shown in figure 2 (c) and (d), before calcinations, average nanofibers size is about 165 nm and that after calcination, it is 60 nm.

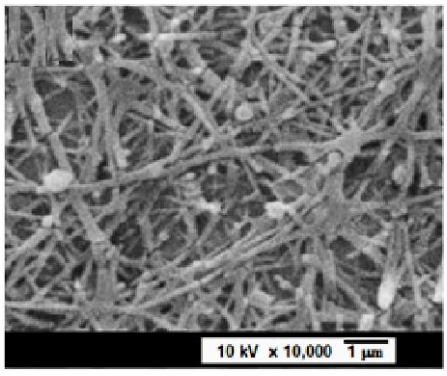


Figure 3 SEM image of (SnO_2-ZnO)/PPy

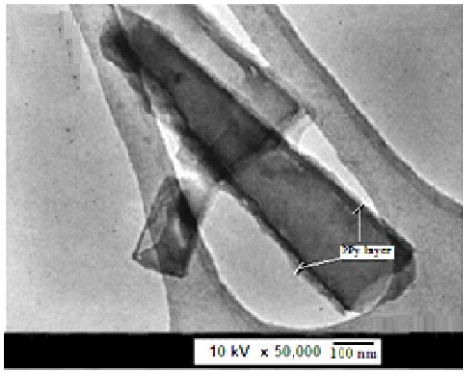


Figure 4 TEM image of (SnO_2-ZnO)/PPy

Morphology of PPy-caoted nanofibers showing similar texture with those of electrospun nanofibers before and after calcination is depicted in figure 2. Figure 4 depicted the TEM of PPy-coated nanofiber which manifested core shell type structure with thin PPy layer. In the study of TEM, nanocables peeled off from the substrate, dispersed in ethanol and exposed to ultrasonic environment of 30 s which causes the shorter length of nanocables. Though the SnO_2-ZnO nanofibers have white colour, they becomes yellowish in $FeCl_3$ ethanolic solution. Further when exposed this solution with pyrrole vapour, it becomes balck, which manifested formation of PPy layer on the SnO_2-ZnO nanofibers. TEM, also exhibited nanofiber's diameter size which was also derived from SEM pictures.

B. Sensitivity Measurement

At different concentration of ammonia gas (15 ppm to 90 ppm), the variation of sensing behavior of resistor type (SnO_2-ZnO)/PPy nanofibers sensor with time is shown in the following figure 5.

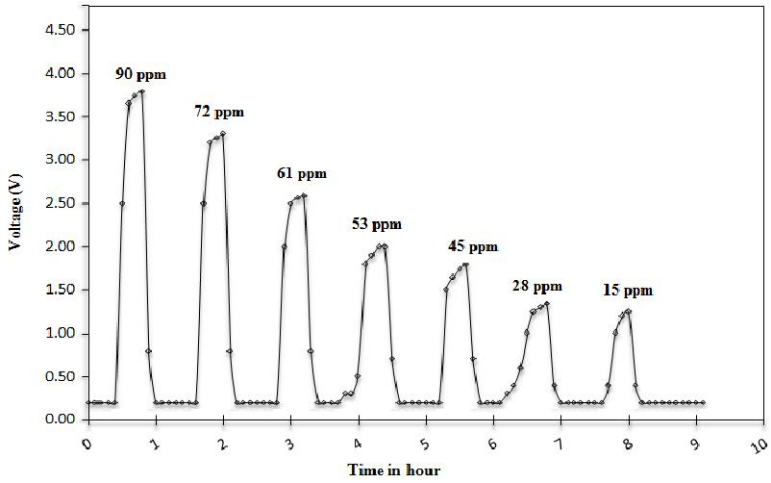


Figure 5 response/recovery features of (SnO_2-ZnO)/PPy nanofibers sensor to NH_3 gas at 300 K

As shown in figure (5), the response of sensor to the varying concentration of ammonia gas is due to the interactions between positive charge along the PPy chains and surrounding environment of NH_3 gas. Redox reaction occurs when PPy is exposed to the NH_3 gas, an electron donating gas. Due to this, decrease in effective number of charge carries causing reduction of its conductance [25]. At different NH_3 concentration, typical response/recovery features of nanocables versus time are depicted in figure (5) at constant current. As shown in response, voltage increases at higher ammonia concentration (say 90 ppm), after about 45 s, it reaches constant value, exhibiting saturation of sensor. Then sensing probe is exposed to air to get recovery of voltage to initial minimum value (0.2 V). for different concentration of NH_3, sensor showed different saturation levels. This feature of sensor can be used to evaluate the sensor response for different gas concentrations. The minimum response time is determined to be 38 s, hence this sensor showed fast response as its surface to volume ratio is large.

Different sensing measurements were carried out and average sensing response is graphed with ammonia gas concentrations which are shown in figure 6.

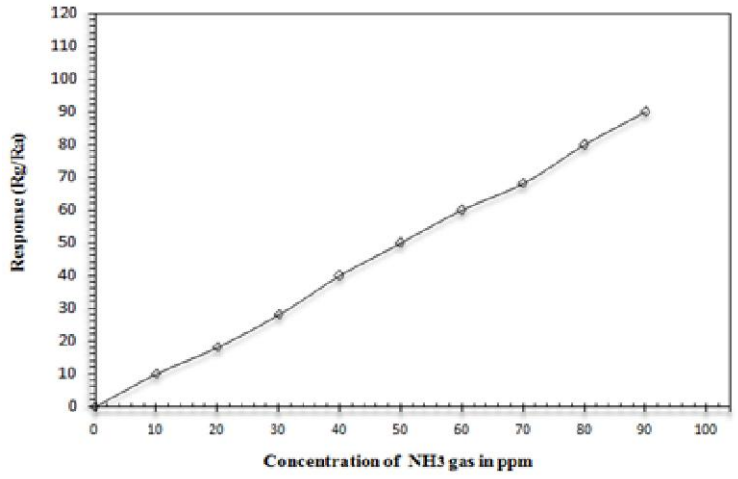


Figure 6 Linear response of (SnO_2-ZnO)/PPy nanofibers sensor to NH_3 gas

As shown in figure 6, as ammonia gas concentration increases, amount of reaction occurring between NH3 and PPy increases, exhibiting involvement of more free electrons along the PPy chains and raising of resistance of the sensor i.e. more response. This linear

response is useful to determine the unknown ammonia gas concentration.

IV. Conclusion

SnO_2-ZnO electrospun nanofibers were prepared via vapor-phase polymerization to use as porous template for polymerizing thin PPy layer and (SnO_2-ZnO)/PPy nanofibers sensor was fabricated to sense NH_3 gas at room temperature (300 K). The fabricated sensor exhibited linear response to ammonia gas which allows for the determination of unknown ammonia gas concentration. SEM and TEM pictures, after calcination exhibited decrease of diameter sizes of nanofibers. Due to high porosity of nanofibers structure, more reactions between NH_3 and the positive charges along PPy chains occur and sensing is enhanced. This more porosity also led to easier diffusion of ammonia gas which exhibit decrease of response and recovery times. The response time is 12 s and recovery time is 38 s. Hence the sensor under study was best among the known sensors. Due to low operating temperature i.e. 300 K (room temperature), its durability is more.

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