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EFFECT OF ANNEALING ON THE GAS SENSING APPLICATIONS OF POLYANILINE (PANI) NANOWIRES

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Abstract- In this work, polyaniline (PANI) nanowires have been successfully prepared using template synthesis technique by chemical polymerisation of aniline within the pores of anodic alumina template. The characterization of annealed and as-prepared samples was done by using Scanning electron microscopy (SEM), X-ray diffraction (XRD) and Source meter. The SEM confirms the wire-like morphology of as prepared and annealed PANI nanowires whereas XRD investigation shows the amorphous nature of as-prepared and annealed PANI nanowires. I-V studies of PANI nanowires show the increase in sensitivity of annealed PANI nanowires towards the gas sensing capability of prepared samples
Keywords: – XRD; SEM; template synthesis; Polyaniline.

1. INTRODUCTION OF POLYANILINE

A tremendous amount of research has been carried out in the field of conducting polymers since 1977 when the conjugated polymer polyacetylene was discovered to conduct electricity through halogen doping [1–3]. The 2000 Nobel Prize in Chemistry recognized the discovery of conducting polymers over 25 years of progress in this field [4, 5]. In recent years, there has been growing interest in research on nanostructured conducting polymers such as polypyrole, Polyaniline, Polythiophene, and their derivatives, etc have attracted the attention of the material scientist, engineers and technocrats due to their wide applications in nanoelectronics [6], optoelectronics [7], photonics [8], sensors [9] and solar cells [10]. Sensors and actuators assembled with conductive polymers nanowires are claimed to have superior responding characteristics to their conventional counterpart. Polyaniline (PANI) is a conducting polymer of the semi-flexible HYPERLINK "http://en.wikipedia.org/wiki/Semi-flexible_rod_polymer"rod polymer family. PAni is a special conducting polymer since its doped state can be controlled by acid/base reactions. This is widely used to detect acidic and basic gases. When exposed in ammonia gas, PAni undergo dedoping by deprotonation [11-16]:

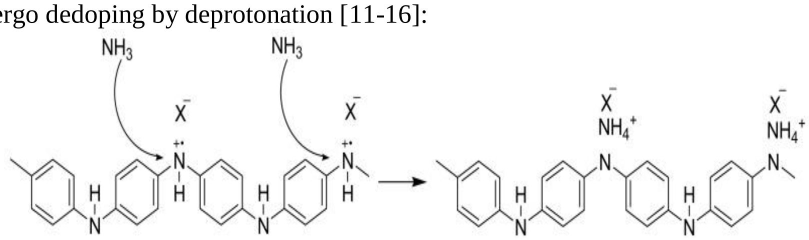

Figure1. Formation of ammonium ions

The protons on −NH− groups were transferred to NH3 molecules to form ammonium ions while PANI itself turned into its base form as shown in Fig.1. This process is reversible, and in fact, when ammonia atmosphere is removed, the ammonium ion can be decomposed to ammonia gas and proton. After reaction with acidic gases, such as HC1, H2S and CO2 (in present of water) PANI will be doped [17-22]. Water is also able to transfer protons to PANI [23]. Weiller et al. reported that H2 can be adsorb on the positive-charged nitrogen atoms of PANI, and then dissociate into hydrogen atoms. The following formation of new N-H bonds between the hydrogen atoms and nitrogens can reduce the resistance of PANI [24]

Amongst the family of conducting polymers and organic semiconductors, polyaniline has many attractive processing properties [25]. A variety of techniques have been used such as thermal evaporation, chemical vapor deposition (CVD), chemical self-assembly, sol-gel process, and template synthesis for the fabrication of nanowires [26 and references therein]. Template synthesis is an elegant approach for the fabrication of 1D structure such as nanowires and nanotubes [26-30]. This technique makes use of porous membrane such as track-etch membrane, anodic alumina oxide (AAO), and mica etc. The desire material can be deposited into the pores of membrane via sol-gel, chemical vapor deposition (CVD), electrochemical deposition, chemical deposition, and electro less deposition. The size and shape of the Nanowires is true replica of pores geometry. In this paper we describe here the fabrication and characterization of carbon nanowires before and after annealing

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process via template-synthesis using Polyaniline (PANI) as a conducting polymer. Indeed, various metal oxide nanowires i.e ZnO nanowires [31-33], CuO/Cu2O Nanowires [34], CoFe2O4 nanowires [35], Na2Ti3O7 nanowires [36], WO3nanowires [37], SnO2 nanowires [38] and Al2O3 nanowires [39] have attracted considerable attention due to their ease of fabrication, clear operating mechanism, high sensing response with good operating stability.

2. EXPERIMENTAL DETAIL

All chemicals purchased from Merck are of analytical grade with high purity. Anodic alumina oxide (AAO) templates of diameter 100nm, thickness 60 micron and pore density 109 pore/cm2 are purchased from what man, USA. Aniline of 0.5 M aqueous solution and Ferric Chloride (FeCl3) of 0.5 M aqueous solution with Dilute Hydrochloric Acid (HCl) are used. AAO membrane with pore size of 100 nm was sandwiched between two O- rings of U shaped glass tubes composed of two compartments. Monomer and oxidant solutions were separated with this membrane in which they diffuse through each other by the way of the pores that the AAO membrane has. After successive polymerization time (3 hours), Polyaniline sample was synthesized by chemical oxidation method using FeCl3 as oxidant. After that membrane was removed and washed with distilled water for several times and the sample was dried in room temperature. In the next step the Annealing of Polyaniline is done. In this process, the high temperature annealing of conducting polymer (Polyaniline) is done at 600oC for 4 hrs using muffle furnace which convert the Polyaniline nanowires into carbon nanowires.

3. CHEMICAL POLYMERISATION MECHANISM

The polymerisation of polyaniline occurs within the pores of anodic alumina template by the oxidant FeCl3. The polymerisation mechanism of conducting polymers is very complex & different researchers have suggested number of explanations about the mechanism. Probably the most accepted polymerisation mechanism of polyaniline as follows the three steps (i) monomer is oxidised losing an electron to form a radical cation (ii) a radical cation react with another radical cation to form a dimer by elimination of two protons (iii) the dimer being more easily oxidised than monomer, will then react further to give higher oligomers, until the oligomer become insoluble & precipitate within the pores of AAO template to form polyaniline nanowires.

4. MORPHOLOGY AND CRYSTAL STRUCTURE

SEM micrograph presents the surface morphology of polypyrrole nanowires as shown in Fig. 2 and Fig. 3. The SEM images of nanowires reveal good quality of deposition however some of the wires seems to be oversized as claimed by WATT-MAN membrane (nanowires are true-replica of pore geometry) which is due to the axial coupling. Due to hydrostatic pressure during the dissolution of the host AAO membrane with NaOH, Bunches of polyaniline nanowires get formed. Nanowires seem to be quite flexible in nature as they are curved. Moreover, the image shows homogeneous nucleation and high porosity which indicates its reliability as sensing material.

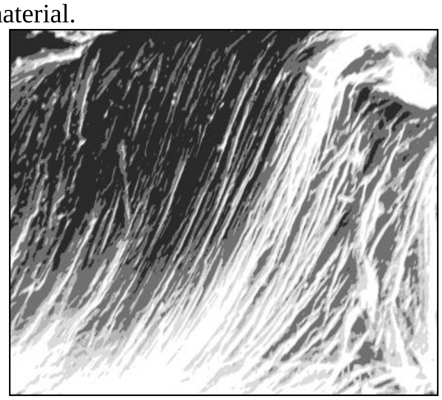


Figure 2. SEM images showing the flexible nature

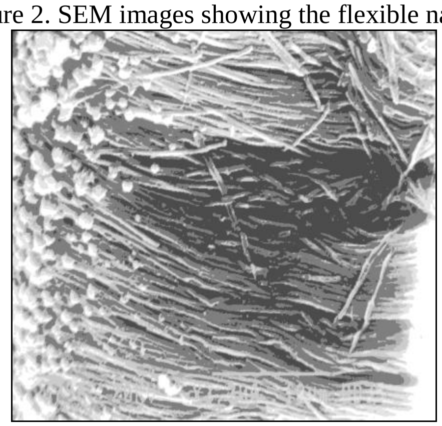


Figure 3. SEM images showing dense fibril structure of polyaniline nanowires.

5. XRD CHARACTERIZATION

X-Ray diffraction study of polyaniline nanowires are carried by Diffractometer system named XPERT-PRO. XRD patterns provide information in relation to the nature and structure of the samples. The results are taken with Start Position [°2Th.]=10.0084 and End Position [°2Th.]=79.9804 with Step Size [°2Th.]= 0.0170 and Scan Step Time [s]= 25.1981 having continuous scanning type. The reading is taken at the Temperature of 25.00°C and with copper as the anode material. The diffraction pattern of polyaniline nanowires before annealed and after annealed indicates the amorphous nature. The diffraction pattern of pure PANI has a broad peak nearly at 2θ = 28o and 360. The XRD pattern of these polymer blends does not show sharp peaks which confirm the amorphous nature of polymer blends. The X-Ray diffraction pattern for polyaniline nanowires before annealed and after annealed are shown in Figure 4 and 5.

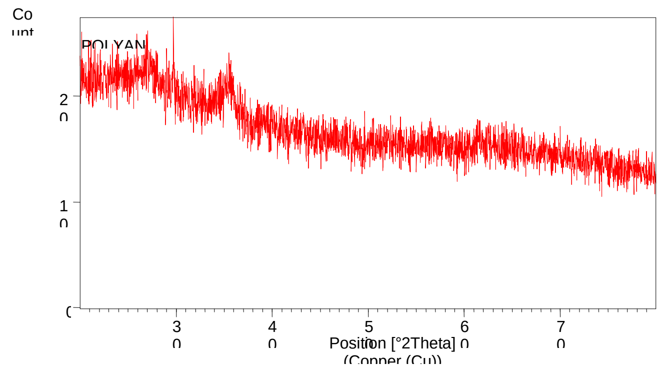


Figure 4. XRD graph of polyaniline nanowires before annealing

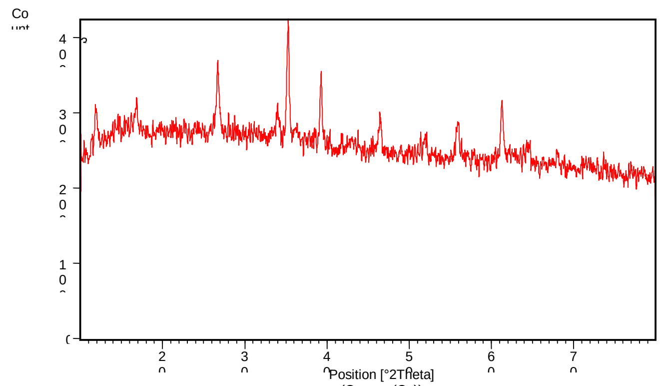
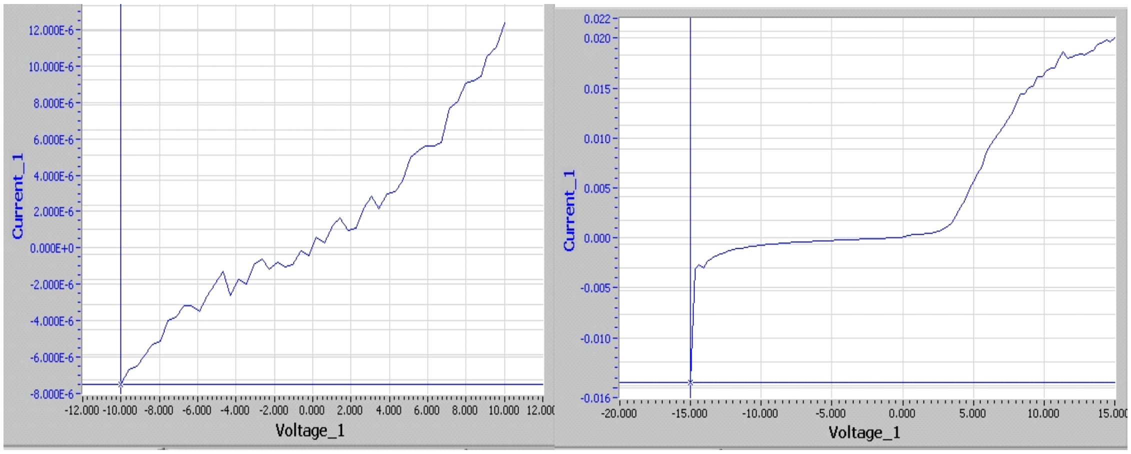


Figure 5: XRD graph of polyaniline nanowires after annealing.

6. ELECTRICAL CHARACTERIZATION

I-V characterization of the prepared conduction Polyaniline is done with the help of KEITHLE SOURCE METER 2420. I-V Characteristics of Polyaniline CNW before and after annealing process is shown in Fig.6. The synthesized polyaniline nanowires sample is sandwiched between the copper films making sure that both the copper film donot get short circuit shown in Fig.7. Then both the negative and positive terminals of the keithle source meter are connected with the copper films. Further the sample sandwiched between the copper films is exposed to various gases for different time period, resulting in the change in the I-V graph. With increase in time of exposure the current also starts increasing, which shows the change in the I-V characteristics when exposed to various gases. In my thesis work, I have used ammonia and benzene gas, which shows different graphs as shown in Fig.8.



Before Annealing After Annealing

Figure 6: I-V Characteristics of Polyaniline CNW before and after annealing process.

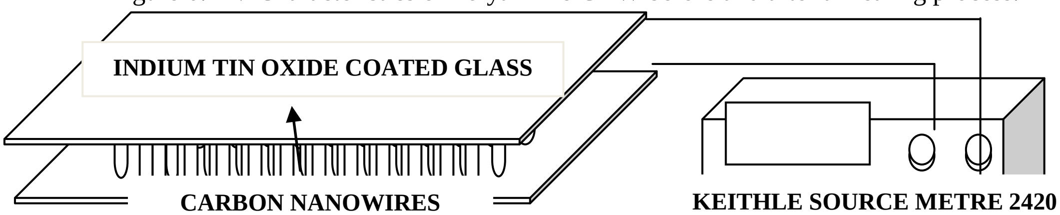
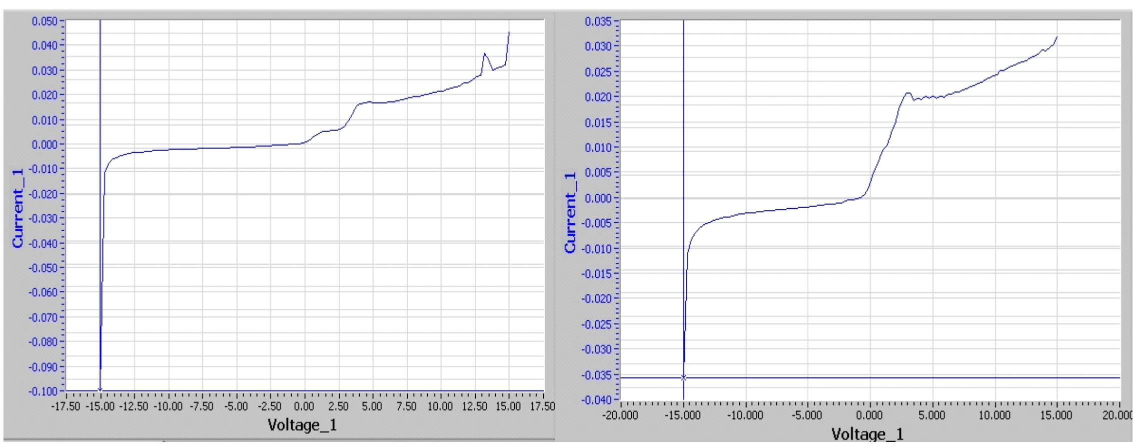


Figure 7: Setup for I-V characterization



For Ammonia Gas For Benzene Gas

Figure 8: I-V Characteristics of annealed Polyaniline CNW when exposed to ammonia and benzene gas vapor for 3 minutes respectively.

These I-V characteristics prove that polyaniline nanowires posse's good sensing capability which can be enhanced to thousand times after annealing and can be used as a sensor material for various applications.

7. CONCLUSION

Template synthesis is an easy approach to fabricate the nanowires. Conducting poly-nanowires can be used as a gas sensor for sensing the various gases and can be applicable to various gases sensing applications. The I-V characteristics of conducting polyaniline nanowires demonstrated that gas sensors based on polyaniline nanowires exhibited good sensitivity towards ammonia and benzene. Further, the template method of synthesis can be employed for fabrication of nanotubes which are composed of different conducting polymers such as polypyrole (PPY), Polythiophene (PT), etc which finds their application in controlled drugged delivery and storage. A dense fibrillar structure of polyaniline nano fibers is clearly evident in the SEM images. SEM images indicate usability of nano fibers as gas sensing applications.

Authors have declared that no competing interests exist.

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