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Synthesis, Characterization and Effect of Ammonia on Polyaniline Doped with HCL

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Abstract—*In this paper, we report synthesis, characterization and ammonia gas sensing study of conducting polyaniline doped with hydrochloric acid. Polyaniline is synthesized through chemical oxidative polymerization route from monomer aniline using ammonium persulphate as oxidizing agent and hydrochloric acid as dopant at room temperature. The Ultra Violet-Visible spectroscopy (UV-vis) and Fourier Transform Infrared Spectroscopy (FTIR) confirms the emeraldine structure of polyaniline. Scanning Electron Microscope (SEM) study reveals rod like shape of synthesized material. X-ray Diffraction (XRD) analysis shows crystalline nature with grain size around 40 nm. As prepared sample is further characterized by Thermo Gravimetric Analysis (TGA) and Energy Dispersive X-ray Analysis (EDAX) techniques. The prepared sample is converted in the form of pellets and their response when exposed to ammonia is studied as chemo resistive type gas sensor by using two probe technique with the help of Keithley 2000 multi meter.*

1. INTRODUCTION

Conducting polymers are a unique class of materials that have been the topic of investigation worldwide for almost three decades for many researchers because of their novel properties such as electrical conductivity, mechanical strength, good environmental stability and ease of synthethesis [1]. These polymers have wide range of applications in various fields such as sensors, anticorrosive materials, plastic solar cells, light emitting diodes and energy storage devises [4,6,8]. Polypyrrol, Polythione, Polyaniline and their derivatives are amongst these polymers under investigation. However, of all these polymers, polyaniline is most popular as it is inexpensive and can be easily synthesized by chemical or electrochemical route [2]. Polyaniline is known to exhibit electric properties which depend upon its different phase, structures and employed synthetic routes [10]. It has been reported as a promising candidate with great potential applications in various fields including humidity and gas sensors [5]. The importance of protection and monitoring of environment is well understood and number of gas sensors has been developed in the past based on metal oxides. However they generally operate at elevated temperature as against conducting polymers which operate at room temperature. In this context, here we report synthesis of conducting polyaniline by chemical oxidative route for its application as an ammonia gas sensor. The synthesized material has been analyzed by various characterization techniques such as FTIR, UV-VIs spectroscopy, X-Ray diffraction and SEM. Its electrical conductivity is measured using two probe technique.

2. MATERIALS AND METHODS

Materials

Aniline (0.1 M, Thomas Baker, $C_6H_5NH_2$, purity 99.5%) used as received. ammonium persulphate (0.1 M, Hexon Laboratories Pvt. Ltd. Pune, $(NH_4)_2S_2O_8$, purity 99%), used as oxidant. Hydrochloric acid (HCl) used as dopant and double distilled water.

Method for Synthesis of Polyaniline

An aqueous solution of Hydrochloric acid and aniline is prepared in a beaker. Ammonium persulphate solution is added drop wise to this solution under constant magnetic stirring and maintaining the temperature at 0°C as the reaction is exothermic. After addition of the oxidant the reaction mixture was left for about 5-6 hours to complete the polymerization process. After polymerization, the deep green colour precipitate is filtered by gravity filtration method several times till the filtrate became colorless. The prepared material is then dried in an oven for about 12 hours. Finally it is crushed into fine powder and converted in the form of pellets with help of a hydraulic machine by applying 5 ton pressure.

3. RESULTS AND DISCUSSIONS

In order to study nature of bonding we characterized sample with Fourier Transform Infrared Spectroscopy (FTIR), the FTIR graph is as shown in Fig. 1.

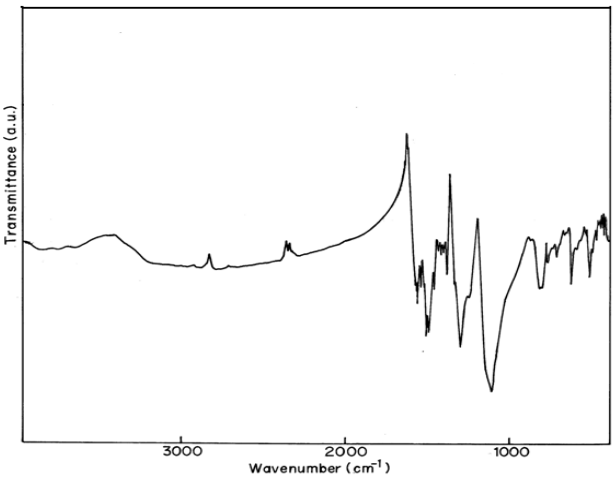

Fig. 1: FTIR Spectra of PANI doped with HCl

The peaks are at wave numbers 1538, 1487, 1420, 1282, 1372, 1102, and 742 cm^{-1}. The peaks at wave numbers 1538 and 1487 cm^{-1} are corresponds to stretching vibration mode for the quinoid (Q) and benzenoid (B) rings and the peak at wave number 1420 cm^{-1} is attributed to C–C aromatic ring stretching of the benzenoid diamine unit. The peak at wave number 1282 cm^{-1} is attributed to C–N stretching and peak at wave number 1102 cm^{-1} is due to N=Q=N stretching. The peak at the wave number 740 cm^{-1} is due to C–H out of plane bending vibrations. The intense peak at 641 cm^{-1} is of C-Cl stretching [13].

The EDAX characterization is carried out to study elemental analysis of the sample. Fig. 2 and Table 1 represents the EDAX analysis.

Table 1: EDAX Table

ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.6728

Element	(keV)	mass%	Error%	At%
C K	0.277	38.67	0.64	47.29
N K	0.392	42.46	3.50	44.52
O K	0.525	0.75	2.24	0.69
Cl K	2.621	18.12	0.27	7.51
Total		100.00		100.00

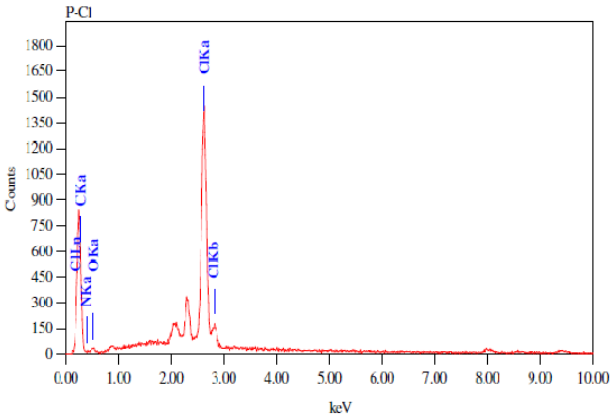

Fig. 2: EDAX of PANI doped with HCl

From the diffracted peaks obtained in the XRD spectrum (Fig. 3), the average grain size of the synthesized PANI particles are determined with the help of the Debye-Scherrer formula. The value of interplaner spacing (d spacing) is calculated by using Bragg's relation. The characteristic peak appeared at 26° corresponding to (200) crystal plane. The grain size is found to be 40 nm and the value of d spacing is 3.45Å. From peak from XRD spectrum, it could be observed that the synthesized material is of semi crystalline nature.

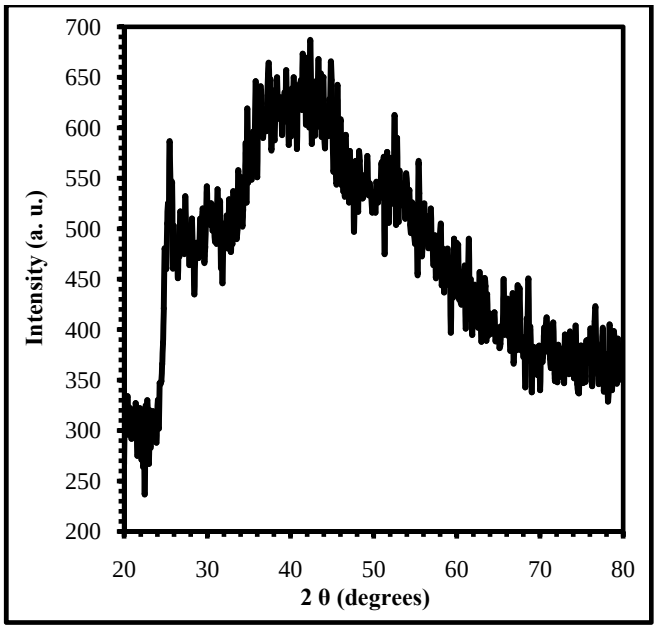

Fig. 3: XRD Spectra of PANI doped with HCl

The surface morphology of as prepared polyaniline doped with HCl sample is studied by SEM characterization. Fig. 4 and Fig. 5 gives SEM image of PANI sample.

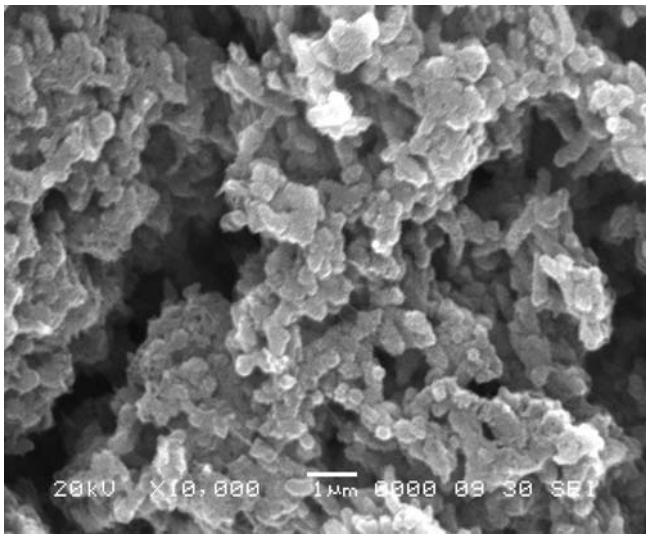

Fig. 4: SEM image of PANI doped with HCl (mag.10000)

The SEM image PANI shows uniform size distribution in tubular form having average size 150 nm. The difference in grain size estimated by XRD and the particle size estimated by SEM suggests that two or more crystallites may be fused together to form a particle.

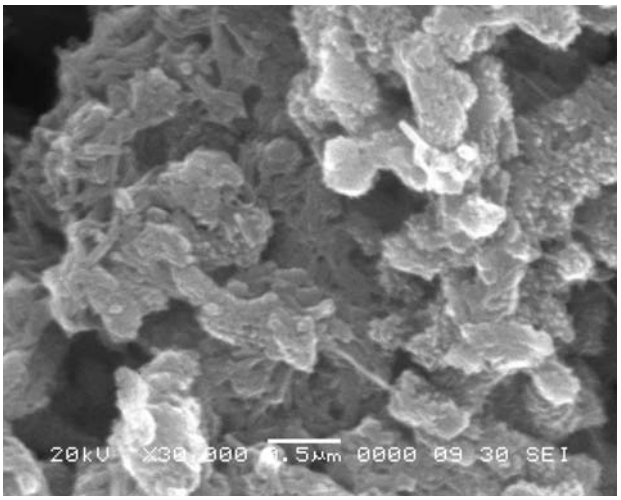

Fig. 5: SEM image of PANI doped with HCl (mag.30000)

The Ultra Violet Visible spectroscopy (UV Vis) is carried out in order to study the electronic transition. Fig. 6 gives UV spectra of prepared sample.

The UV spectra shows two characteristics absorption peaks at 324 nm and 616 nm. These are assigned to polaron/bipolaron transition that occurs in doped PANI**.** [11] The band energy for these peaks is estimated to be 3.82 eV and 2 eV.

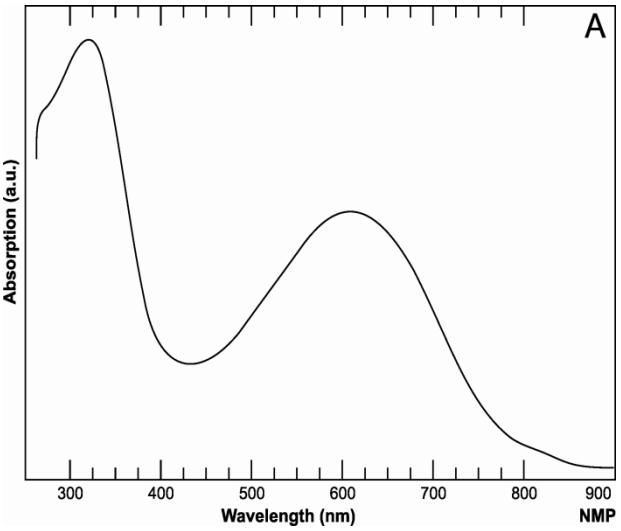

Fig. 6: UV Spectra of PANI doped with HCl

In order to study the thermal stability the sample is characterized by TGA technique. Fig. 7 gives TGA graph of PANI. From graph, it could be observed that the weight losses are may be due to loss of the moisture, loss of dopants and loss of polymer.

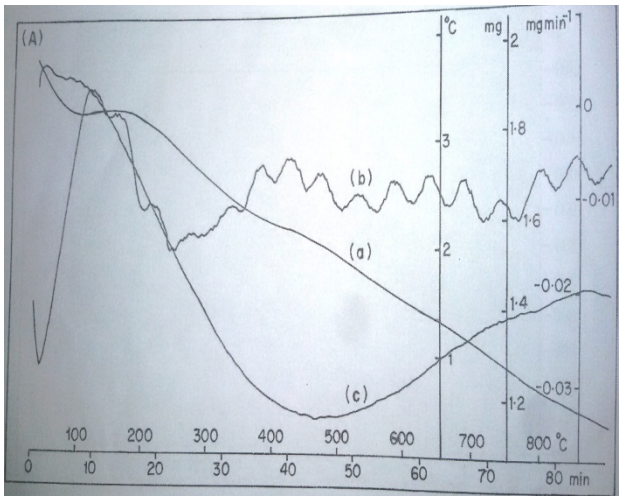

Fig. 5: SEM image of PANI doped with HCl

The electrical resistance of the PANI doped with HCl sample is determined as a function of exposing time of ammonia gas. The sample in the form of pellet of diameter 12 mm is placed into the glass chamber; 100 ppm ammonia gas is passed into the chamber. The gas sensitive characteristics are investigated by recording resistance when pellet is exposed to ammonia at room temperature. The several gas sensing cycles are recorded in order to investigate the response of PANI doped with HCl sample to ammonia.

The significant change in electrical resistance of PANI sample was observed when it was exposed to ammonia vapours as shown in Fig. 8. The sensing mechanism is governed by the protonation / deprotonation phenomena. It showed that resistance of the material increases when it was exposed to ammonia. For every sensing cycle material showed same response. The resistance of PANI sample increased because of the undoping or the reduction of charge carriers by adsorption of ammonia on the surface of pellet.

Ammonia gas molecules withdraw protons from N^{+}–H sites to form energetically more favorable NH^{4+} due to which PANI was changed from the emeraldine salt state to the emeraldine base state, leading to the reduced hole density in the PANI and thus an increased resistance. When the pellet was exposed to air; the reversible nature was recorded. NH^{4+} decomposes to form NH^{3} and resistance recovered.

For first cycle the initial resistance of PANI sample was 26218.87 ohm. When 100 ppm ammonia gas was exposed to pellet, the resistance of pellet was recorded as 3175959 ohm and when pellet was exposed to air, the resistance got decreased to 1074758 ohm. On repeating sensing cycles with constant ammonia concentration, it was observed that the initial resistance went on increasing. The initial resistance

could not come back to original value. This could be due to the trapping of ammonia molecules on surface of the sample.

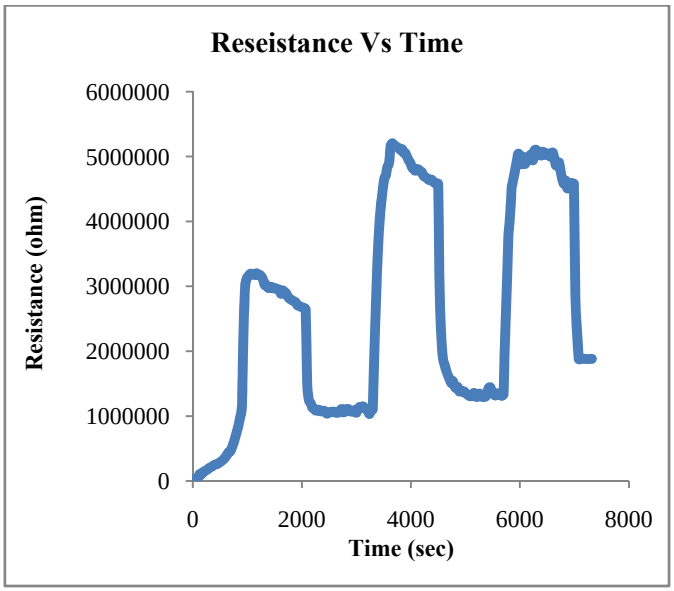

Fig. 8: Resistance response of PANI doped with HCl to 100 ppm ammonia gas.

4. CONCLUSIONS

The conducting polyaniline doped with HCl has been successfully synthesized by chemical oxidative route. The morphological study (XRD and SEM) indicates the as prepared sample is in nano region. The FTIR characterization reveals the exact formation of PANI. From gas sensing studies it could be observed that PANI doped with HCl could be a good candidate for sensing ammonia gas at room temperature however further studies of sensing at low ppm level are required.

5. ACKNOWLEDGEMENT

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