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Study of conducting polyaniline as formaldehyde sensor

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Abstract
Formaldehyde is a carcinogenic VOC and its extensive usage in household and industries leads to overexposure. As per WHO statement, exposure limit of formaldehyde should not exceed 0.78 ppm per 30 min. The present work reports the study of doped polyaniline (PANI) as a formaldehyde sensor at room temperature. The polyaniline was synthesized by chemical oxidative polymerization from monomer aniline and ammonium persulfate (APS) as an oxidant and HCl, $HClO_4$ and HNO_3 acid as dopants. The prepared doped polyaniline samples were characterized using XRD, SEM and FTIR characterization technique. Subsequently, the prepared polyaniline samples were developed in the form of pellets for formaldehyde sensing studies. A two-probe gas sensing assembly was built to monitor the resultant changes in electrical resistance on exposure to formaldehyde (2 ppm) at room temperature. It was inferred that Polyaniline doped with HNO_3 exhibits a good candidature for Formaldehyde sensing.

Keywords: formaldehyde, polyaniline, VOC, WHO.

1. Introduction

Formaldehyde is a volatile organic compound (VOC) that is used in the manufacturing process of various products which include glues, resins, plywood, insulating materials, fabrics and pulp and paper products. Formaldehyde is also an important chemical solvent because of its application in dry cleaning solutions, cosmetics, fabrics, and cleaning products. Due to extensive usage, formaldehyde is absorbed through the skin and eyes or inhaled, which may cause eye, nose and throat irritation, breathing difficulties, coughing, sneezing, nausea, and may sometimes lead to even death. The World Health Organization (WHO) states that the concentration of formaldehyde over a 30 min. period should be less than 0.78 ppm (WHO, 2001), which seeks the attention of researchers to sense formaldehyde.

The conductive properties of polymers, such as polyaniline and its derivatives are used by attaching electrodes to the polymer chain forming a chemiresistor in the circuit and the resistivity of polymer is measured. These polymers act as sensors which detects the change in resistivity caused due to adsorption or absorption of a VOC's. Among the conducting polymers, polyaniline can be easily synthesized and processed and has good sensitivity and selectivity towards some gases at room temperature than inorganic semiconductor sensors. Polyaniline also has high electrical stability and is capable of sensing over a wide range of analyte concentrations; hence it can be used as a formaldehyde sensor.

In this paper, we present the synthesis and characterization of Polyaniline doped with dopants viz. Hydrochloric acid (HCl), Perchloric Acid ($HClO_4$) and Nitric acid (HNO_3) and the formaldehyde (HCHO) sensing properties of Polyaniline doped with HNO_3.

2. Experimental

Chemical oxidative polymerization synthesis technique was used to synthesize the Polyaniline from monomer aniline. Appropriate amount of aniline was dissolved in acidic medium viz. Hydrochloric acid (HCl), in an aqueous solution kept in an ice bath at 0-5 °C. Ammonium persulphate (APS) was added dropwise to the prepared solution for oxidation along with stirring using a Teflon coated magnetic stirrer at constant rpm which maintained the pH level of the solution. A low temperature surrounding was maintained throughout the reaction. This reaction was continued till the dark green colored viscous product was obtained. This obtained product was emeraldine salt (ES) which is half oxidized state of PANI. The obtained product was filtered several times using gravity filtering technique followed with washing by distilled water and diluted acid until the filtrate became colorless. The precipitate procured in the end was kept in an oven for drying and sintered at 50 °C for 48 hrs. At the end of reaction, green

Colored powders of polyaniline doped with HCl were obtained.

A similar process was followed for the synthesis of Polyaniline doped with Perchloric acid ($HClO_4$) and Nitric acid (HNO_3). In this process, all physical and chemical factors affecting the synthesis process were kept constant. This lead to synthesis of desired product viz. Polyaniline doped with Hydrochloric acid (HCl), Perchloric acid ($HClO_4$) and Nitric acid (HNO_3).

3. Characterization

3.1 X-ray Diffraction

The XRD characterization of PANI doped with 3 acid dopants were carried out in the 2θ range of 200-800 degree. Following figures 1 a], 1 b] and 1 c] shows the XRD pattern of PANI-HCl, PANI-$HClO_4$ and PANI-HNO_3 respectively.

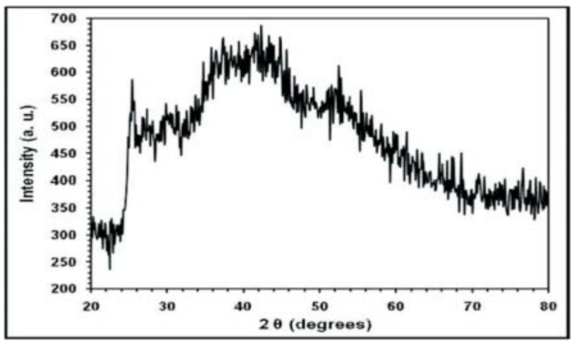

Fig 1: a] XRD of PANI-HCl]

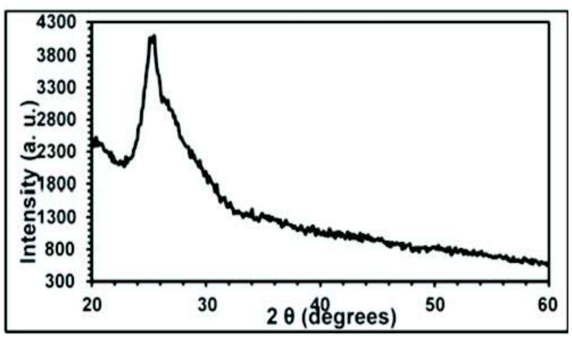

Fig 1: b] XRD of PANI-$HClO_4$

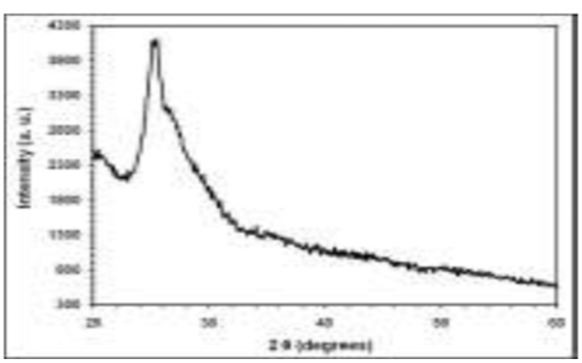

Fig 1: c] XRD of PANI-HNO_3

3.2 SEM

The surface morphology of the PANI doped with different acids were studied using SEM characterization technique. Following figures 2 a], 2 b] and 2 c] shows the SEM images of PANI-HCl, PANI-$HClO_4$ and PANI-HNO_3 respectively.

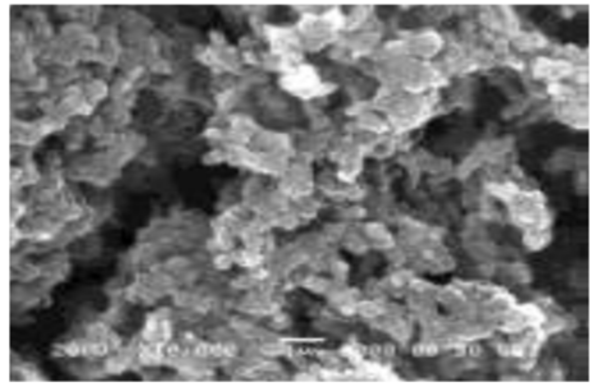

Fig 2: a] SEM of PANI-HCl

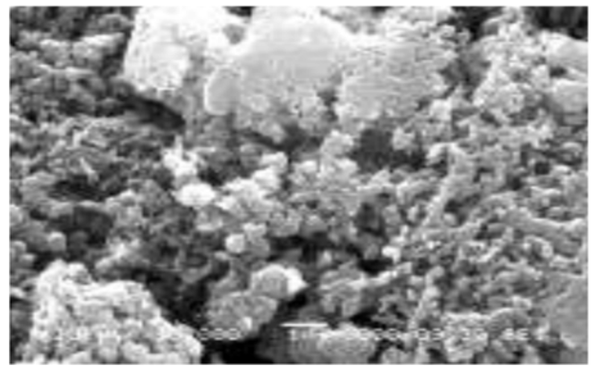

Fig 2: b] SEM of PANI-$HClO_4$

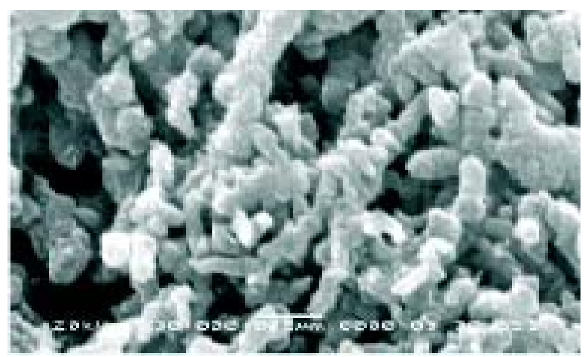

Fig 2: c] SEM of PANI- HNO_3

3.3 FTIR

The prepared samples were analyzed using FTIR spectrometer having range $400 cm^{-1}$ to $4000 cm^{-1}$. Following figures 3 a], 3 b] and 3 c] shows the FTIR spectrum of PANI-HCl, PANI-$HClO_4$ and PANI-HNO_3 respectively.

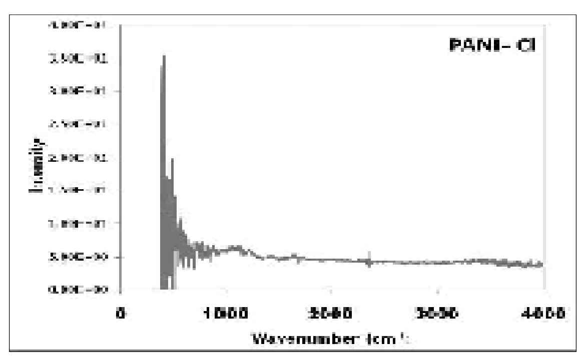

Fig 3: a] FTIR of PANI-HCl

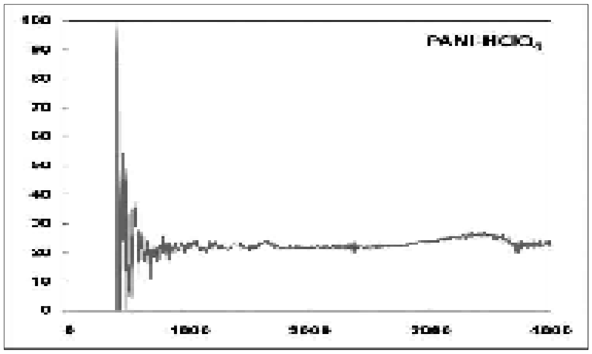

Fig 3: b] FTIR of PANI-HClO4

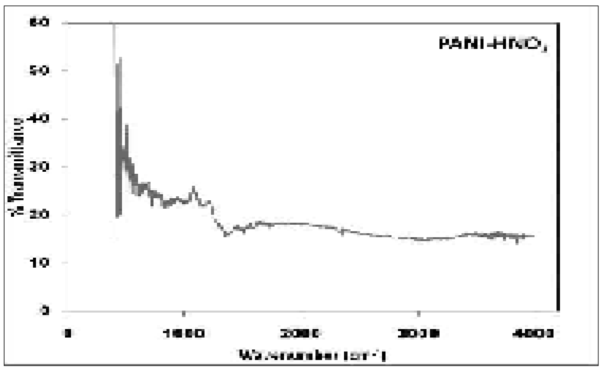

Fig 3: c] FTIR of PANI-HNO4

4. Formaldehyde Sensing Studies

The obtained green colored powder of polyaniline doped with HCl, $HClO_4$ and HNO_3 were then developed in the form of pallets through a hydraulic press for the sensing studies of formaldehyde. The pellets were developed at an optimized condition of 2 ton pressure and time of 2 minute. These pellets had diameter of 12mm and thickness was 1 mm. In the formation of pellet, 320 mg powder of PANI was utilized. A two-probe gas sensing assembly was built for sensing studies. This assembly had electrodes made up of copper which were kept at a constant distance of 7mm from each other. To study the resultant changes, pellets were kept in the assembly and resistance in the air (R_a) of pellet were measured over a fixed period of time. Then through a micropipette, 2ppm of formaldehyde was introduced in the assembly and the change in resistance (R_g) was monitored until it reaches a saturation state. Response time (T_R) is measured as 90% of time required to reach the R_g. Once the saturation is achieved, pellet was again exposed to air and the time required to reach its initial resistance value was measured. In similar fashion, recovery time (T_S) were measured for the sensor.

5. Results and Discussion

5.1 XRD

Following table gives the 2θ, interplanar distance (d), crystalline size for the synthesized samples.

Sample	2θ (degree)	d (Å)	Crystalline size(nm)
PANI-HCl	25.46	3.49	64.94
PANI-HClO4	25.36	3.51	44.98
PANI- HNO3	25.10	3.55	7.1

5.2 SEM

Figure 2 a] shows the SEM image of PANI-HCl. It shows that it has spherical morphology with varying grain size. The average grain size is found to be 91.63 nm. Figure 2 b] shows the SEM image of PANI-$HClO_4$. It shows the nanostructured morphology. Figure 2 c] shows the SEM image of PANI-HNO_3. It confirms the nanostructured morphology with average grain size 20.66 nm.

5.3 FTIR

Figure 3 a] shows the various peaks of PANI-HCl. In the spectra 1690 corresponds to C=O stretching, 1487 benzoid ring stretching band. 1340 is due to C-N stretching of tertiary amine.
Figure 3 b] shows peaks in PANI-$HClO_4$. The peak of 3293 due to N-H stretching. 1562 is for stretching of quinoid ring. 672 is for C-Cl stretching.
Figure 3 c] shows peaks in PANI-HNO_3. Peak 1365 is due to bending of quinoid ring. Peak 1360 is for N-O symmetric stretch while peak 626 corresponds to NH_2 wagging.

5.4 Formaldehyde Sensing Studies

Figure 5.4 a] shows the resultant electrical changes of the resistance of the PANI-HNO_3 on the exposure of 2 ppm of formaldehyde. The response time of the sensor was observed to be 69 sec while the recovery was very shorter of 22 sec. The sensitivity was calculated to be 78.57%.

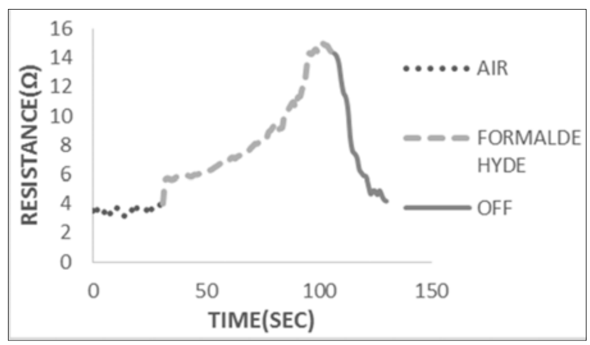

Fig 5.4: a] Formaldehyde sensing graph

6. Conclusion

PANI doped with acids such as HCl, $HClO_4$ and HNO_3 was synthesized successfully and characterized by standard characterization techniques. The effect of different dopants on the synthesis is studied. The sensing behavior of PANI-HNO_3 is studied which confirmed that it exhibits a good candidature for formaldehyde sensing at lower ppm level at room temperature.

7. References

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