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Synthesis and Characterization of Polyaniline, using Different Dopant, for Sensing Application of Pollutant Gases

Research Article

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Abstract. Conducting polymers have been attracting considerable attention of researchers worldwide since 1980, due to their unique electrical, optical, thermal and magnetic properties. Among these polymers, polyaniline (PAni) is most popular as it can be synthesized for specific applications like rechargeable batteries, bio-sensors, corrosion paintings, organic electronic materials, EMI shielding, light emitting diodes etc. In this paper, we report synthesis of conducting polyaniline using different dopants such as HCL, $HCLO_4$, HNO_3 and H_2SO_4 by oxidative chemical polymerization of aniline. The synthesized polyaniline materials were characterized by Fourier Transform Infra-red Spectroscopy (FTIR), Powder X-Ray Diffraction (XRD), Energy Dispersive X-ray analysis (EDAX) and Ultra-Violate (UV-VIS) Spectroscopy techniques.

Keywords. Conducting polymer; FTIR, Gas Sensor; Dopant

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1. Introduction

Since 1980, conducting polymers have been the center of attraction, of many researchers, as they open up numerous possibilities of generation of novel materials with diverse applications in the field of chemical sensing, storage devices, electromagnetic interference (EMI) shielding, organic light emitting devices, microwave absorption, corrosion devices etc. [1–5]. Among the other conducting polymers such as polypyrrole, polythiophene, polyacetylene, polyaniline and their derivatives etc., polyaniline (PAni) is the most promising candidate, due to its wide range of tunable properties derived from its structural flexibility. PAni exhibits unique redox chemistry and a large spin density resulting into interesting electrical and magnetic properties. Moreover, PAni possesses good environmental stability, can be conveniently synthesized in aqueous solution and organic solvents, the monomer is inexpensive and easily available [6]. Thus, PAni has received much attention because of its novel properties and potential applications. The literature dealing with the synthesis of conducting polymers by different methods suggests that their properties are highly dependent on the dopant used, the concentration of doping level and the structure of polymer formed [8].

PAni can be synthesized from the monomer aniline either by oxidative chemical polymerization [9,10] or by electrochemical polymerization [11,12]. The electrochemical reaction is carried out either in one compartment or in two compartment electrochemical cell in aqueous medium or in a suitable solvent [13]. The present article deals with the synthesis of PAni by the chemical oxidative polymerization method, by using different acids as dopants and ammonium peroxydisulphate as an oxidizing agent. The acids used for doping are HCl(A), $HClO_4$(B), HNO_3(C) and H_2SO_4(D). All the reaction conditions were maintained, except the dopant, in order to investigate the effect of dopant on the prepared polymer. The PAni synthesized by using these acids as dopants were characterized by XRD, FTIR and UV-VIS spectroscopy.

2. Experimental Details

Chemical oxidative polymerization of Aniline has been done in an aqueous solution at (0-5 °C) by dissolving aniline monomer in an acidic medium of various inorganic acids as HCl, $HCLO_4$, HNO_3 and H_2SO_4 as dopant one by one. In a typical procedure for chemical polymerization of monomer aniline, to form conducting polyaniline, an appropriate amount of 0.1 M aniline was dissolved in the pre calculated amount of dopant acid. An aqueous solution of proper amount of ammonium peroxydisulphate, which acts as an oxidizing agent, was added to this solution, drop by drop, under constant magnetic stirring for 10-12 hours.

The reaction being exothermic in nature, it was maintained at low temperature throughout completion of polymerization. After the polymerization completed, a dark green coloured precipitate was obtained. The green colour confirmed the conducting emeraldine salt form of polymer. The precipitate thus obtained on filtration was washed with dilute acid followed by distilled water several times until the filtrate became colorless. The precipitate thus obtained was dried at 60 °C in an oven for 12 hours to obtain free flow PAni powder, which was further used for physio-chemical characterization study using XRD, FTIR, EDAX and UV-VIS spectroscopy techniques.

3. Results and Discussions

Figure 1 shows UV-VIS spectra of PAni-HCl It can be noticed that the characteristic band of PAni appears at 337 nm which can be attributed to π to π^* transition. The band gap energy is calculated to be 3.82 eV which is in agreement with reported value [17]. Figure 2 shows UV-VIS spectra of PAni-HClO4 shows two peaks at 320 and 810 nm suggesting π to π^* and pi to polaron transition. Figure 3 shows UV-VIS spectra of PAni-HNO_3. It shows two peaks at 310 and 411 nm which can be assigned to π to π^* transition and localized polaron which are characteristic of Protonated PAni. Figure 4 gives UV-VIS spectra of PAni-H_2SO_4.It has two peaks at 320 and 415 nm suggesting pi to π^* and π to polaron transition [17].

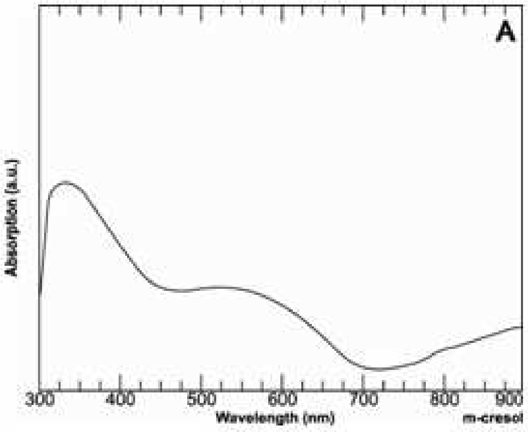


Figure 1. UV-VIS spectra of PAni-HCl

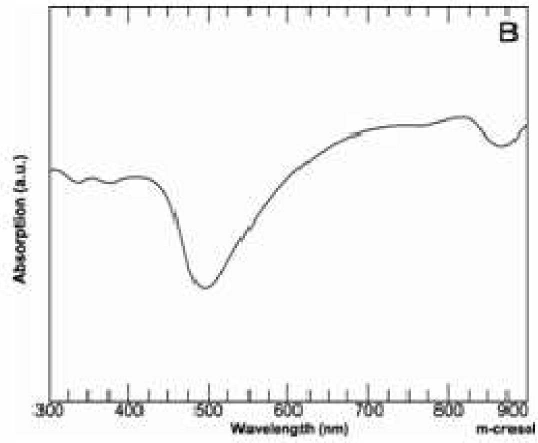


Figure 2. UV-VIS spectra of PAni-HClO4

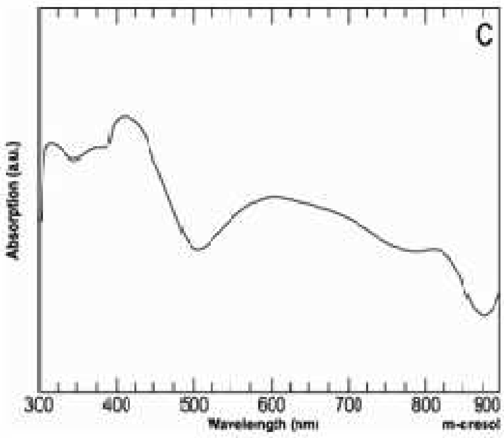


Figure 3. UV-VIS spectra of PAni-HNO_3

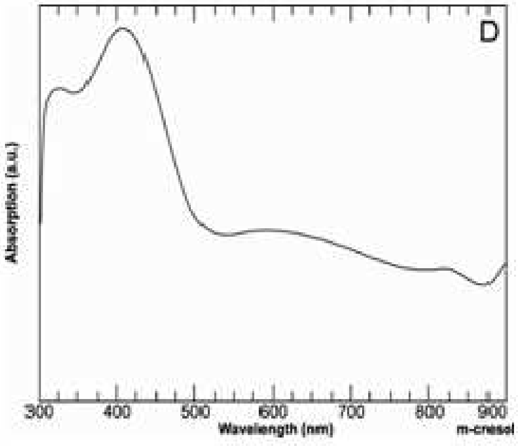


Figure 4. UV-VIS spectra of PAni-H_2SO_4

Figure 5 shows XRD of PAni-HNO_3 which has a sharp peak at 260 indicating crystalline nature of prepared sample. Figure 6 is XRD of PAni-H_2SO_4 having a sharp peak at 24.60 suggesting crystalline form of prepared sample. Figure 7 gives XRD of PAni HCl. It has a peak at 24.80 and suggests semi crystalline nature of the prepared sample. Figure 8 is FTIR of PAni HCl and PAni $HCLO_4$. The major peaks are at 1581 cm^{-1} (C-N stretch of the Quinoid unit of PAni), 1487 cm^{-1} (C-C stretch of the Benzenoid unit of PAni) and 1102 cm^{-1} (Quinoid unit vibration of doped PAni) which agree with the peaks reported earlier [18–21].

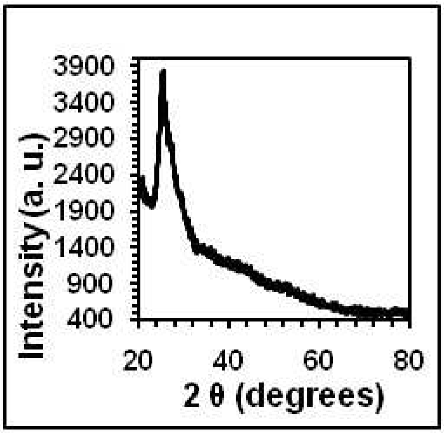


Figure 5. XRD PAni-HNO_3

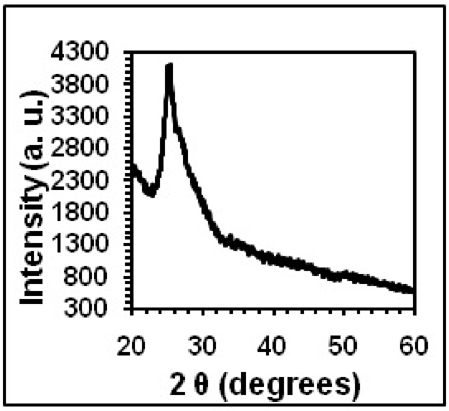


Figure 6. XRD PAni-H_2SO_4

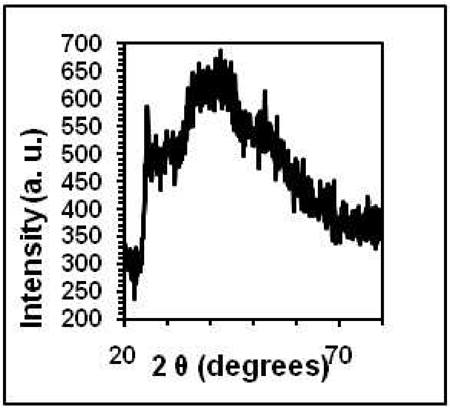


Figure 7. XRD PAni-HCL

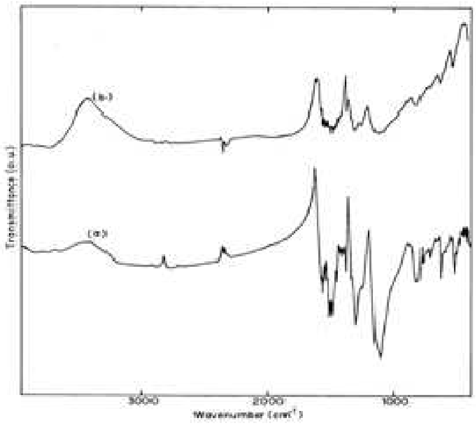


Figure 8. FTIR a-PAniHCl b-PAniHCLO4

Figure 9 gives FTIR of PAniHNO_3 and PAniH_2SO_4. The major peaks observed are at $750\,cm^{-1}$ (out of plane vibration of benzene group), $1025\,cm^{-1}$ (C-H in plane bending of 1, 4-ring), $1500\,cm^{-1}$ (C-C stretching mode for Benzenoid), 1300 cm^{-1} (bending mode for Quinoid unit) [22, 23].

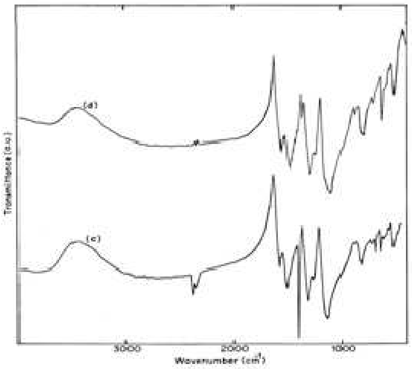


Figure 9. FTIR c-PAniHNO3 d-PAniH2SO4

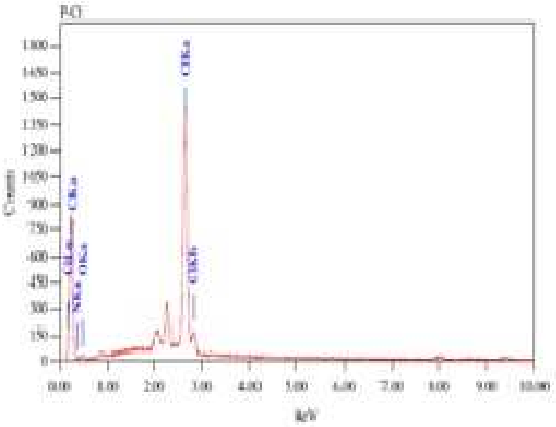
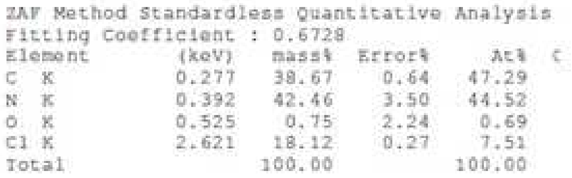


Figure 10. EDAX PAni-HCl



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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.6728
Element        (keV)    mass%   Error%     At%  C
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
```

Figure 11. Readings EDAX PAni-HCl

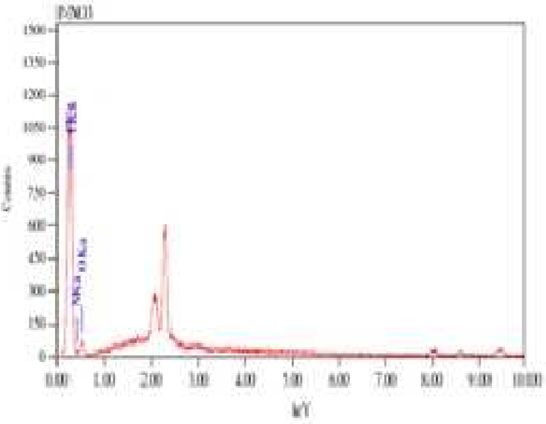
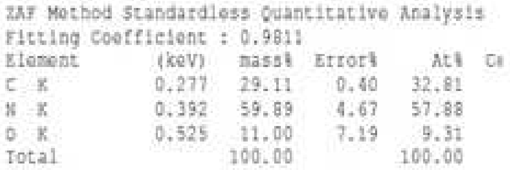


Figure 12. EDAX PAni-HNO_3



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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.9811
Element        (keV)    mass%   Error%     At%  C
C   K          0.277    29.11     0.40   32.81
N   K          0.392    59.89     4.67   57.88
O   K          0.525    11.00     7.19    9.31
Total                  100.00           100.00
```

Figure 13. Readings EDAX PAni-HNO_3

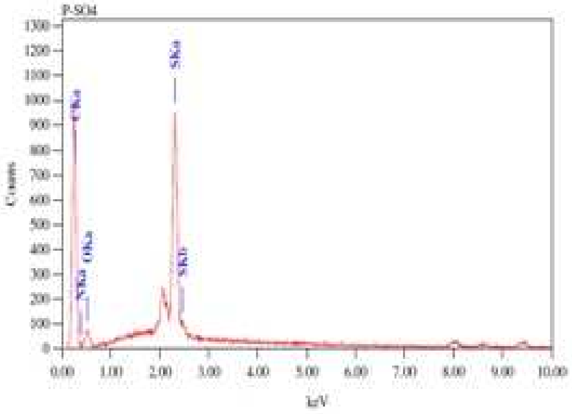
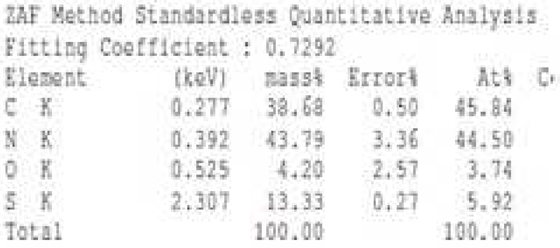


Figure 14. EDAX PAni-H_2SO_4



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ZAF Method Standardless Quantitative Analysis
Fitting Coefficient : 0.7292
Element        (keV)    mass%   Error%     At%  C
C   K          0.277    38.68     0.50   45.84
N   K          0.392    43.79     3.36   44.50
O   K          0.525     4.20     2.57    3.74
S   K          2.307    13.33     0.27    5.92
Total                  100.00           100.00
```

Figure 15. Readings EDAX PAni-H_2SO_4

4. Conclusion

We have successfully synthesized conducting PAni using various acids as dopant. The synthesized polymers have been characterized using UV-VIS, FTIR, EDAX and XRD spectroscopic techniques. The FTIR analysis confirms the chemical structure of PAni. The crystalline nature of PAni is observed from XRD patterns. UV-VIS spectra confirm the formation of conjugated polymers. EDAX spectra confirm the elemental analysis of synthesized polymers.

The characterization study of synthesized polymers reveal that the nature of dopant plays an important role on the structural formation of polymer, its electrical conductivity and in turn its gas sensing property.

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Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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