

SYNTHESIS AND ELECTRICAL CONDUCTIVITY STUDIES OF BENZENE SULFONIC ACID-DOPED POLYANILINE*

BY

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Abstract— In this present work, A series of benzene sulfonic acid-doped polyaniline (PANI) were synthesized by chemical oxidative polymerization. The formation of benzene sulfonic acid-doped polyaniline (PANI-BSA) composited was characterized by various methods like, UV– visible absorption spectroscopies, Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) respectively. And the effects of benzene sulfonic acid (BSA)-doping concentration on the electrical conductivity's were discussed. The effect of dopant on the kinetics of polymerization has been studied by UV–VIS spectroscopy. The presence of oxalic acid in the polymer has been studied by FT-IR, and morphology by SEM. The results display that an increase in benzene sulfonic acid -doping concentration will lead to a trend of first increase and then decrease in the electrical conductivity. The maximum electrical conductivity can reach $3.89 \times 10^{-2} \text{ S.cm}^{-1}$ when benzene sulfonic acid-doping concentrations is 0.75 M. It was found that the conductivity of PANI-BSA composites is higher than undoped polyaniline

Keywords— dopant, benzene sulfonic acid, polyaniline, conductivity

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1. Introduction

Nowadays, the conducting polymers have emerged as a new class of materials because of their unique chemical, electrical and optical properties. By proper doping the conductivity of these conducting polymers can be changing from semiconducting to metallic phase, which suggestions new concept of charge transport mechanism. Among different conducting polymers, conductive polyaniline has been studied widely because of its environmental stability its easy of synthesis in aqueous media, special electrical, optical and other properties. The conductive polyaniline is a suitable

candidate for a variety of technological applications such as electromagnetic shielding, solar cells, sensors and electrodes for rechargeable batteries. [1–13].

In this work, we report the electrical conductivity by two-probe method of these synthesized samples (doped polyaniline and undoped polyaniline) has been studied. The FT-IR spectra UV-visible absorption spectroscopies, SEM have been carried out to characterize these samples.

2. Experimental details

2.1 Synthesis of undoped polyaniline (UPANI)

Undoped Polyaniline has been synthesized by in situ oxidative polymerization of aniline and APS as oxidant. The oxidant monomer ratio is 1: 1.25. An APS and aniline were dissolved in 200 mL round bottom flask and stirred 12 hrs well. After that the green precipitate was filtered, washed with distilled water and acetone for several times respectively and finally dried in oven for 60°C at 12 h.

2.2. Synthesis of doped polyaniline at different benzene sulfonic acid concentrations (PANI-BSA)

The PANI samples were prepared by chemical oxidative polymerization. A 0.25 M aqueous solution of ammonium persulfate (APS) and 0.2 M of aniline were dissolved in 50 mL and 20 mL benzene sulfonic acid (BSA) solution of certain concentration (0.25 M, 0.5 M, 0.75 M, 1.0 M, and 1.5M) respectively. Then, the mixture was stirred 12 hrs. After that the green precipitate was filtered, washed with distilled water and acetone for several times respectively and finally dried in oven for 60°C at 12 h.

3. Results and discussion

In the UV-vis spectra as shown in Figure 1, the undoped sample exhibits two strong absorption peaks at 327 nm and 610 nm, corresponding to the π - π^* transition of benzenoid rings and quinoid rings respectively [44]. For the doped PANI, these two peaks redshift to 330 nm and

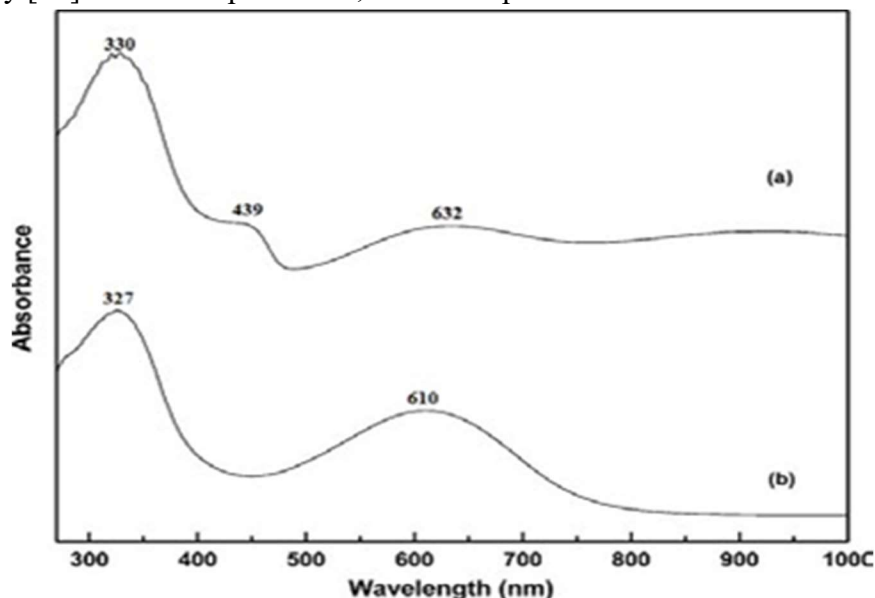


Fig. 1. UV-vis spectra of (a) doped PANI with BSA concentration at 0.75M and (b) undoped PANI 632 nm respectively with the intensity of the latter peak decreasing dramatically, which further confirms occurrence of the protonation at the imine nitrogen sites [45]. Moreover, both the new

absorption peak at 439 nm in the doped sample are assigned to the polaron band transition [46] caused by doping

Figure 2 shows FT-IR spectra of the UPANI and PANI doped with different concentration (0.75M, PANI- BSA).

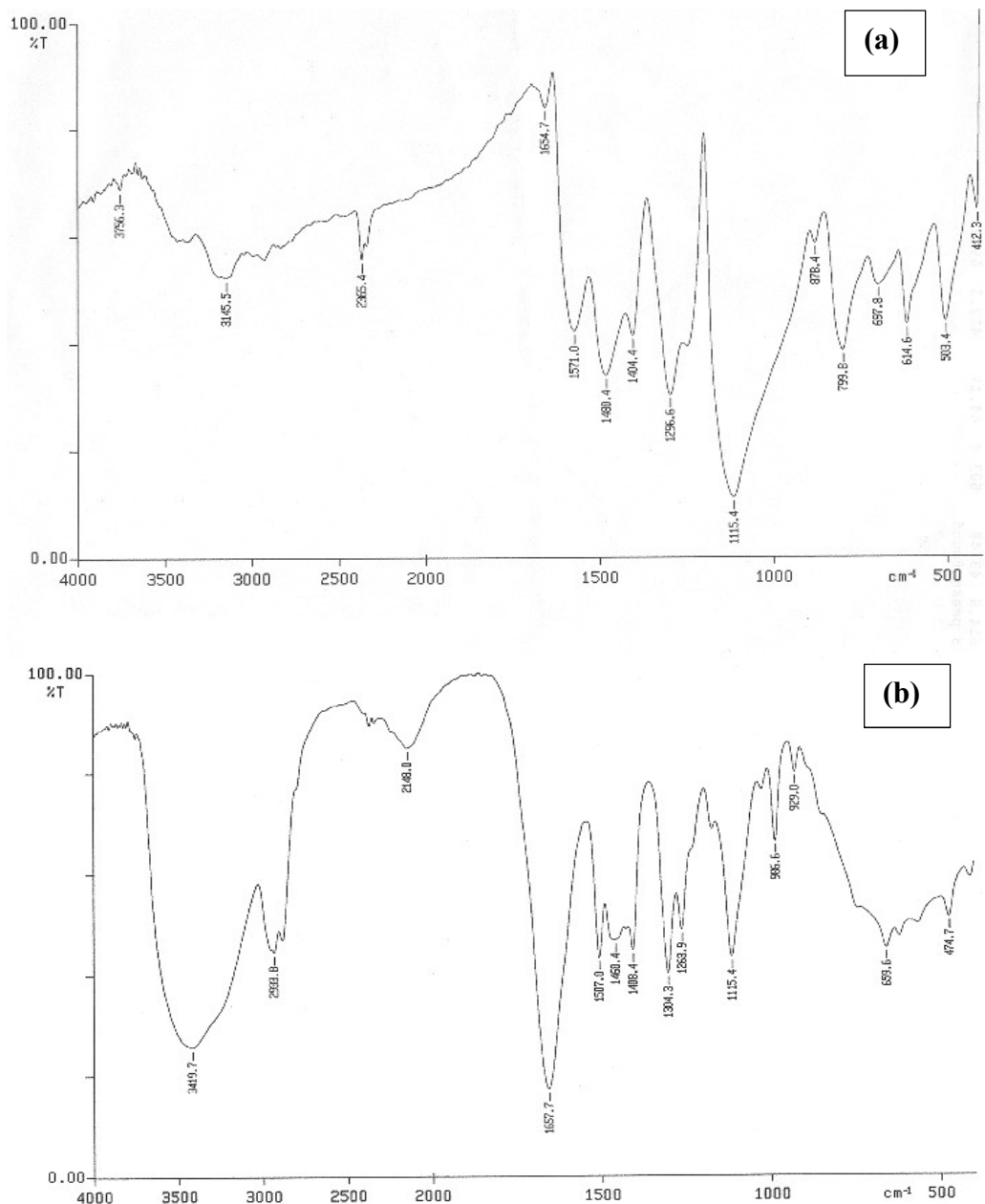


Fig. 2. FTIR spectra of (a) undoped PANI and (b) doped PANI with BSA concentration at 0.75 M

The FT-IR spectroscopy is a powerful instrument for analyzing the oxidation state of PANI and the molecular structure [14, 15]. As can be seen from Figure 1, for both the samples, the absorption peak positions of 3165-3443 cm^{-1} , 1560-1570 cm^{-1} , 1480-1490 cm^{-1} , 1302-1304 cm^{-1} , 1243- 1245

cm^{-1} , $1108\text{-}1119\text{ cm}^{-1}$, $800\text{-}805$ and $819\text{-}822\text{ cm}^{-1}$ are the same. The absorption band observed at 1587 cm^{-1} is related to the quinone structure and that at 1471 cm^{-1} is characterized via benzene ring stretching. An intensity ratio of the absorption peak position at 1587 cm^{-1} to that at 1471 cm^{-1} is a quantitative measurement of the oxidation state of PANI [14].

Figure 3 displays the SEM image of the doped PANI powder synthesized at 0.75 M BSA concentration. It can be observed that plate shaped PANI particles are gained with the diameter of 100 nm and length of 300–400 nm.

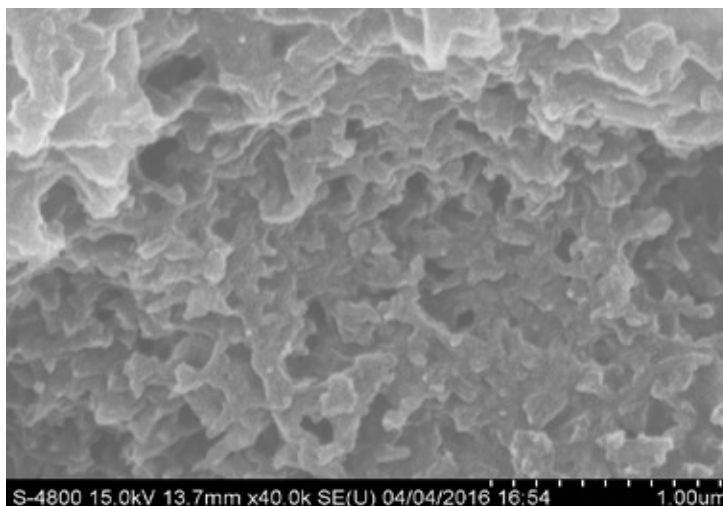


Fig. 3. SEM image of BSA (0.75M) doped PANI powder

Before Conductivity measurement, the all samples (doped PANI prepared at 0.25 M, 0.5 M, 0.75 M, 1.0 M, and 1.5M BSA concentration and UPANI) were pelletized at 7 tons for 1 min using a Carver hydraulic press. Sufficiently thin samples of ~ 1 mm were derived. The conductivity measurements were carried out by a two-probe technique recorded by a multimeter (Keithley model 2001).

Conductors generally show ohmic behavior wherein the voltage across the material varies linearly with the current and the I-V plot has a constant slope, which is the resistance of a material. This means that the current density linearly increases with the applied electric field. It can be observed that resistance of the samples.

The specific resistivity has been evaluated as,

$$\rho = RA/L \quad (1)$$

$$\text{OR conductivity, } \sigma = 1 / \rho \quad (2)$$

Where ρ is its resistivity, A is the cross sectional area of the sample and L is its thickness. The effect of dopant ion on the overall conductivity behaviour of polyaniline was observed. This indicates that all samples behave as ohmic conductors. Shown in Table 1 are values of the electrical conductivity of undoped and doped polyaniline samples.

Ob no	M (BSA)	Conductivity (S/cm)
1	undoped sample	0.09×10^{-4}
2	0.25	0.9×10^{-2}
3	0.50	2.15×10^{-2}
4	0.75	3.89×10^{-2}
5	1.0	1.56×10^{-2}
6	1.5	1.05×10^{-2}

Table 1. PANI conductivity values of BSA with various concentrations.

The differences in conductivity values are due to the effect of dopant ions. As can be seen, the undoped sample has conductivities in the range of 10^{-4} , which makes the sample highly insulating typical of a normal polymer. The highest conductivity (3.89 S/cm) was obtained for the BSA -doped sample; the lowest conductivity (0.09 S/cm) was exhibited by the undoped sample. The room temperature conductivity for undoped sample was found to be 0.09×10^{-4} S/cm for undoped samples while it increased to a value of 3.89 S/cm for BSA doped samples

4. Conclusion

The Doped PANI were synthesized with addition of hydrochloric acid by chemical oxidative polymerization. The doped state was confirmed by a combination of IR spectra and UV-vis spectra. The optimum BSA doping concentration in polyaniline is 0.75 M with a conductivity value of 3.89×10^{-2} S.cm⁻¹

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