Short Communication

Comparative study of pure polyaniline with various oxidants by a template free method

S. Ashokan a, V. Ponnuswamy a,*, P. Jayamurugan a,b

a Department of Physics, Sri Ramakrishna Mission Vidyalaya College of Arts and Science, Coimbatore, Tamil Nadu, India
b Department of Physics, Adhiyamaan College of Engineering, Hosur, Tamil Nadu, India

1. Introduction

Polyaniline is one of the most promising conducting polymers with enhanced conductivity, good environmental stability, easy doping control and diverse color changes corresponding to oxidation levels [1]. Much research has focused on the influence of the polymerizing conditions on the general properties of conducting polymer (chemical, electrochemical, physical, electrical, mechanical, and morphological characteristics).

Recently, a simplified template-free method was proposed to synthesize PANI nanostructures. It can be easily doped upon exposure to a protonic acid and become electrically conductive.

In particular, polyaniline and its derivatives are intrinsically conducting polymers that have been extensively studied during the last twenty years because of their environmental stability (air, moisture), good process ability and their relatively low cost [2,3].

Photoluminescent conducting polymers have attracted much attention because of their potential applications in biosensors [4–9].

In our previous work, we have reported a comparison of the optical property of polyaniline using various dopants by a chemical oxidation method [10]. There are only a few reports concerning photoluminescent and photoconductivity of polyaniline. In this present work, our aim was to make a comparative study among the three oxidants by investigating their photoconductivity behavior.
and photoluminescence properties in polyaniline by the template-free method.

2. Experimental methods

2.1. Materials

Aniline monomer (Sigma-Aldrich, India) was purified by using distillation plant and the oxidants APS (Ammonium peroxydisulfate), $K_2Cr_2O_7$ (Potassium dichromate), FeCl$_3$ (Ferric Chloride), methanol, and acetone (Merck) were purchased for synthesis and used as such.

![Fig. 1. SEM images of (a) APS doped PANI, (b) $K_2Cr_2O_7$ doped PANI and (c) FeCl$_3$ doped PANI.](image1)

![Fig. 2. UV-spectra of (a) APS, (b) $K_2Cr_2O_7$ and (c) FeCl$_3$ doped PANI (inset shows band gap energy).](image2)
2.2. Synthesis by the template-free method

In a typical synthesis, 0.5 M of aniline was dissolved in 150 ml of deionized water and then 20 ml of 0.5 M Ammonium peroxide sulfate (APS) aqueous solution was added to the mixture with constant stirring. The polymerization reaction was carried out under static conditions at room temperature for 24 h. The same process was continued with various oxidizing agents, K2Cr2O7 and FeCl3 with respect to aniline monomer. Excess methanol was poured to stop the reactions. This preparation was kept unagitated for 24 h to settle down the polyaniline powder and the synthesized solution was filtered out under vacuum and washed with methanol, acetone and distilled water several times to remove impurities. Thus prepared samples were dried for 24 h at 60 °C in a vacuum oven. Finally the synthesized samples were ground and the fine powder of PANI was obtained.

2.3. Characterization

The synthesized PANI was characterized by various characterization techniques such as SEM, XRD, FT-IR, UV, photoluminescence and electrical conductivity studies.

A JEOL JSM-5610 Scanning Electron Microscope was used to study the doped aniline surface morphology of the prepared polyaniline powder. The UV–visible spectrum of polyaniline with different oxidants was recorded by employing a Jasco-530 dual beam spectrometer. FT-IR analysis was done in the range 400–4000 cm⁻¹ using a thermo Nicolet V-200 FT-IR spectrometer by KBr pellet technique. X-ray diffraction patterns of polyanilie were recorded using an X-ray diffractometer with CuKα radiation (λ = 1.54 Å) to identify the crystalline nature of the samples. The luminescence spectrum of the PANI was studied by using a FP-6500 spectrofluorometer-67 at room temperature (30 °C). The conductivity measurement for the PANI powder was done by employing a Keithley 6517B electrometer using Four Probe-Setup (DFP.2 model) in the voltage range 0.1–1 V. The dielectric studies of polyaniline were carried out using a Hioki 3532-50 LCR meter at various temperatures in the frequency range 50 Hz to 5 MHz. The photoconductivity measurement of the PANI powder was done by using the

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Fig. 3. FTIR spectra of (a) APS doped PANI, (b) K2Cr2O7 doped PANI and (c) FeCl3 doped PANI.

Fig. 4. XRD patterns of (a) APS doped PANI, (b) K2Cr2O7 doped PANI and (c) FeCl3 doped PANI.

Table 1 XRD patterns of pure polyaniline.

Fig. 5. PL spectra of (a) APS doped PANI, (b) K2Cr2O7 doped PANI and (c) FeCl3 doped PANI.
Keithley 6517B electrometer. PANI pellets were taken and thin copper wires were connected on both sides of the sample with the aid of silver paste (Electronic Grade). A halogen lamp (100 W) containing iodine vapor and tungsten filament was used as a radiation source for the photocurrent measurement.

3. Results and discussion

The SEM photographs of polyaniline doped with APS, K$_2$Cr$_2$O$_7$ and FeCl$_3$ oxidants are shown in Fig. 1a, b and c, respectively. The APS doped PANI composite as a uniform surface with good agglomeration and small sphere-like structure is shown in Fig. 1a. Fig. 1b shows the glassy clear surfaces of K$_2$Cr$_2$O$_7$ and Fig. 1c shows the FeCl$_3$ doped aniline, revealing the flower and layer morphology [11,12]. Thus, the SEM results elucidate that the reactions are remarkably effective on the oxidants for the PANI.

Fig. 2a, b and c shows UV absorption spectra of PANI doped APS, K$_2$Cr$_2$O$_7$ and FeCl$_3$ oxidants, respectively. Fig. 2a shows that the absorption bands at 241 nm and 359 nm are due to the excitation of benzene in the polyaniline chain.

Fig. 6. I–V characteristics of (a) APS doped PANI, (b) K$_2$Cr$_2$O$_7$ doped PANI and (c) FeCl$_3$ doped PANI.

Fig. 7. Temperature vs. resistivity and conductivity of (a) APS, (b) K$_2$Cr$_2$O$_7$ and (c) FeCl$_3$. 
The peak at 359 nm is attributed to $\pi - \pi^*$ benzenoid transition in the leucoemeraldine segments in near ultraviolet region. The two broad absorption bands located at approximately 414 nm and 416 nm are assigned to the polaron $\pi - \pi^*$ transition in emeraldine salt in the visible region. The optical energy gap ($E_g$) could be obtained from the intercept of $h\nu$ vs. $(\alpha h\nu)^2$ (inset Fig. 2a–c) for the PANI sample. The calculated band gap energy for the different oxidants follows: APS > FeCl$_3$ > K$_2$Cr$_2$O$_7$ as 2.7 > 2.5 > 2.3 eV. The higher wavelength of transition enhances the intrinsic conductivity of the samples [13].

FTIR spectra of PANI doped with APS, K$_2$Cr$_2$O$_7$ and FeCl$_3$ oxidants are shown in Fig. 3a, b and c, respectively. The characteristic absorption peaks of PANI at 3216–3436 cm$^{-1}$ are assigned to different types of intera- and inter-molecular hydrogen bonded N–H stretching vibrations of secondary amines. The peak at 2925 cm$^{-1}$ is assigned to the vibrations associated with N–H in the benzenoid ring. The characteristic new peak at 1580 cm$^{-1}$ corresponds to C=C stretching mode of the quinoid rings and the broad band at 1292 cm$^{-1}$ is attributed to C–H in plane deformation vibrations. The peaks at 1042 and 617 cm$^{-1}$ are related to the S=O and S–O stretching vibrations of the sulfonate groups attached to the aromatic rings [14,15]. Especially, the presence of SO$_2^-$ group is confirmed from the appearance of a band around $\sim$08 cm$^{-1}$ in the spectrum of the PANI [16,17].

The X-ray diffraction patterns of polyaniline doped with APS, K$_2$Cr$_2$O$_7$ and FeCl$_3$ oxidants are shown in Fig. 4a, b, and c, respectively. The FWHM, $2\theta$ and ’d’ spacing of these peaks were measured for all the pure polyaniline samples, and their values are given in Table 1. In each case the X-ray diffraction pattern of PANI has a broad peak at about $2\theta \approx 25.9^\circ$ and the three overlapping sharp peaks at 16°, 20° and 22° imply the amorphous structure of polyaniline [18,19]. The crystalline peaks and amorphous corona of the angular intensity profile are used to estimate the percent crystallinity of the polymer systems [20].

Fig. 5a, b and c shows the photoluminescence spectrum of PANI doped with APS, K$_2$Cr$_2$O$_7$ and FeCl$_3$ oxidants, respectively. The APS doped polyaniline depicts a spectrum with
high photoluminescence intensity. The additional sharp peaks at 330 nm, 391 nm and 510 nm lead to longer wavelength of K2Cr2O7 and FeCl3 doped polyaniline. The direct band gap energy value was calculated by using the formula $E_g = \frac{hc}{\lambda}$, where $h$ is a constant ($6.634 \times 10^{-34}$ J/s), $c$ is the velocity of light ($3 \times 10^8$ m/s) and $\lambda$ is the emission wavelength in emission spectrum. The calculated band gap energy value of the APS doped PANI is found to be 3.76 (APS). The mechanism of green emission is mainly due to the concentration of free electrons and the oxidation associated with the process that could have easily formed out of the recombination centers that resulted.

$I-V$ characteristics of the APS, K2Cr2O7 and FeCl3 doped polyaniline are shown in Fig. 6a, b and c, respectively. The thickness of the pellet is 2.434 mm. The samples were sandwiched between copper electrodes with the help of a pressure contact [21]. The current was measured with respect to the applied voltage across the sample at different temperatures. The resistivity at different temperatures is calculated using the following equation:

$$\rho = 4.5324V(d/l)F$$

where $F = d/l$, $I$ is the current, $V$ is the voltage, $d$ is the thickness of the pellet (2.434 mm), $F$ is the correction factor and $S$ is the distance between two probes, and the distance of the probe is 2 mm. The conductivity was calculated using the relation $\sigma = 1/\rho$, where $\rho$ is the resistivity; the correction factor depends on the sample geometry, thickness, borders and location of points in the sample. From Fig. 6a–c, it is noted that current linearly increases with voltage and temperature, which confirms the ohmic behavior. APS doped polyaniline in an aqueous medium shows high conductivity and the current is linearly increasing with applied voltage with respect to temperature and is shown in Fig. 6a. The maximum conductivity $4.68 \times 10^{-7}$ S/cm is obtained for APS doped PANI and the same is found to decrease with a variety of oxidants as shown in Fig. 7. It is also observed that conductivity changes due to the oxidant’s nature.

Fig. 8a–c shows the photocurrent and dark current for the applied input voltage which shows the positive photoconductivity nature of the prepared PANI. It is due to the reduction of charge carriers in the presence of radiation. As a result, when the sample is exposed to light irradiation, the recombination of electrons and holes takes place with a decrease in the number of charge carriers, thus increasing the positive photoconductivity as shown in Fig. 8 [22]. In photocurrent and dark current study, K2Cr2O7 doped PANI shows better response than other oxidants. The AC conductivity characteristics of APS, K2Cr2O7 and FeCl3 oxidants doped polyaniline are shown in Fig. 9a, b and c. The prepared PANI pellets were treated with good quality silver paste to obtain good ohmic conduct when placed between the copper electrodes for the measurements. The dielectric constant of the material is calculated using the following equation:

$$e_r = Cd/\varepsilon_0A$$

where $C$ is the capacitance and $d$ is the sample thickness, $A$ is the cross sectional area of the sample and $\varepsilon_0$ is the free space permittivity ($8.85 \times 10^{-12}$ F/m). Fig. 9 shows that the dielectric constant increases with temperature. The dielectric constant is very high at low frequency range and becomes stable at higher frequency range. This may be due to the presence of the four polarizations namely electronic, ionic, orientation and space charge polarization. The low value of the dielectric constant at high frequency may be due to the significant loss of these polarizations (Fig. 10). The AC conductivity of the PANI is calculated by the
following equation:

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan \delta \quad (3)$$

where $\varepsilon_0$ is the permittivity of the free space, $\varepsilon_r$ is the dielectric constant of the sample, $\tan \delta$ is the dielectric loss and $\omega$ is the angular frequency ($\omega = 2\pi f$). From Fig. 9 (inset), it is observed that AC conductivity increases with temperature. In this present work the maximum conductivity obtained in the aqueous medium (Fig. 11) is for the APS doped polyaniline sample.

4. Conclusion

PANI was prepared by the template-free method of aniline with APS, $K_2Cr_2O_7$ and FeCl$_3$ oxidants. The FT-IR spectra confirm the presence of PANI functional groups. Especially, the presence of SO$_2^-$ group in the APS doped PANI confirms the stability. SEM images reveal the formation of glassy and flower or layers-shaped particles in the samples of PANI with the effects of three oxidants. The optical absorption band around 285–350 nm is due to the $\pi - \pi^*$ electronic transition in the benzene rings present in the polymer backbone. The calculated band gap energy lies between 2.3 and 2.7 eV. The excitation wavelengths of PANI are 330 nm,
391 nm and 510 nm and the mechanism of green emission is mainly due to the concentration of free electrons and the oxidation associated with the process initiated by recombination centers. The dielectric constant is very high at low frequency range and becomes stable at higher frequency. The increased conductivity is due to the formation of better charge transport network in PANI and the maximum electrical conductivity is observed for APS doped PANI. Among the oxidants used the best result was obtained for APS. The investigation of APS doped polyaniline was confirmed by their stability and suitability for humidity sensor, biosensor and optoelectronics. In this work new results regarding photoconductivity and optical properties of polyaniline doped with various oxidants are reported.

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References
