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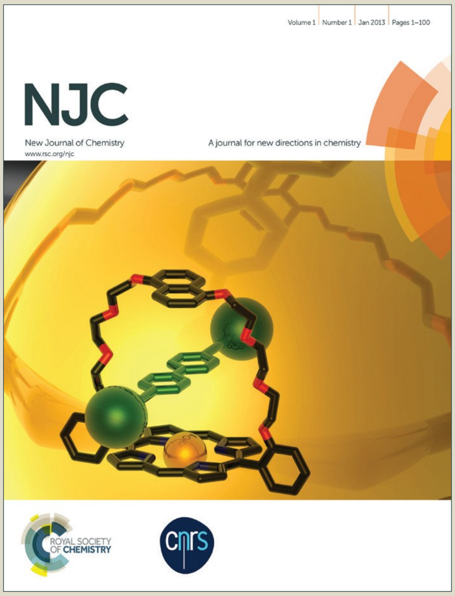

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ARTICLE

# A novel process of alcohol promoted polymerization of aniline to form nano fibrous, fluorescent and highly crystalline polyaniline salt

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Polyaniline salts are being prepared with the use of acids by the oxidation of aniline using ammonium persulfate. Aim of this work is to avoid the use of acids in the preparation of polyaniline salt, which is acidic in nature. The synthesis was carried out by the oxidation of ammonium persulfate in presence of alcohol, β-naphthol, without using any acids. This novel polyaniline salt contains dual dopants of β-naphthol and sulfuric acid. Sulfuric acid group was generated from ammonium persulfate during the oxidation of aniline. This synthesis procedure gave nano sized fiber form of polyaniline salt having crystalline nature with optoelectronic and fluorescence property.

## 1. Introduction

Polyaniline belongs to the conjugated class of organic conducting polymers. Among the conducting polymers, polyaniline (PANI) has attracted much attention because of its properties like ease of synthesis from easily available monomer, controllable electric conductivity, simplicity in doping and de doping, chemical stability, good environmental stability, mechanical flexibility, low cost, and shows various applications. Application of polyaniline such as sensors,[1] electro chromic devices,[2] light-emitting diodes,[3] solar cells,[4] rechargeable batteries,[5] super capacitors,[6] fuel cells,[7] anticorrosion coatings,[8] actuators,[9] membranes,[10] adsorbents,[11] catalysts,[12] etc. have been covered in a review by Gordana C´ iric´ -Marjanovic[13] (references therein). In the same review, acids used in the polymerization of aniline such as sulphuric, hydrochloric, phosphoric, perchloric, acetic, succinic, d,l-tartaric, citric, 3,5-dinitrosalicylic, 5-sulfosalicylic, camphorsulfonic, dodecylbenzenesulfonic, and lignosulfonic acids in the polymerization of aniline have also been covered. Polyaniline salts have also been prepared using polymeric acids such as poly(styrene sulphonic acid),[14,15] poly(vinyl sulphonic acid), and poly(acrylic acid).[15]

Fluorescence properties of few polyaniline systems have been reported in the literature such as polyaniline-fluoroscein,[16] polyaniline-perylenetetracarboxylic acid,[17] polyaniline base prepared from polyaniline-hydrochloride salt[18] and Polyaniline-meso-tetrakis(4-sulfonato phenyl) porphyrin.[19]

The conductivity of polyaniline salts depends on its oxidation degree and doping efficiency.[20] PANI has three basic oxidized structures (leucoemeraldine, emeraldine, and pernigraniline) with different oxidation states, which are chemically and electrochemically switchable. The base form of PANI, emeraldine base (EB) electrically non conducting due to an empty conduction band, but doping with a strong acid protonates imine nitrogen and forms PANI salt, i.e., emeraldine salt, which is electrically conducting.

Polyaniline salts are generally being prepared by the oxidation of aniline in the presence acid. Aniline has been oxidized by ammonium persulfate to PANI-$H_2SO_4$ with and without using $H_2SO_4$.[21,22] Conductivity of PANI-$H_2SO_4$ prepared without using acid is lower than that of the salt prepared with sulfuric acid.[21] This is due to increase in oxidation level and doping level by sulfuric acid. In this work an alcohol, β-naphthol, is used to increase the conductivity of polyaniline salt instead of using sulfuric acid. Alcohol is used for the first time instead of protic acids. This polyaniline salt containing dual dopants of sulfuric acid and β-naphthol groups shows

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DOI: 10.1039/x0xx00000x

highly crystalline, nano fibrous morphology with fluorescent and optoelectronic properties.

## 2. Experimental

### 2.1 Materials

Aniline (SD fine chem, India) was vacuum distilled prior to use, β-Naphthol (sigma Aldrich), chloroform, ammonium persulphate and sulfuric acid (Rankem India) were used as received. Distilled water was used for the all the reaction.

### 2.2 Synthesis of polyaniline-β-napthol-sulfate

In a typical synthesis, 1 ml aniline (11 mmol) and β-naphthol (0.5, 1, 2, 4 mmol) were dissolved in 15 ml of chloroform. Freshly prepared solution of 2.8 g of ammonium persulfate (12.3 mmol) in 30 mL of water was added drop wise into the organic solution through the side of the beaker at ambient temperature. The reaction was continued under 5 $^{0}$C in a refrigerator for 24 h. The obtained deep-green product was filtered, washed with an ample amount of water and acetone. The sample was dried at 50 °C till a constant weight. In this work, these samples are designated as PANI-BN0.5-$H_2SO_4$, PANI-BN1-$H_2SO_4$, PANI-BN2-$H_2SO_4$ and PANI-BN4-$H_2SO_4$.

Polyanililne-sulfate salt (PANI-$H_2SO_4$) was prepared by the above procedure without the use of β-naphthol.

### 2.3 Characterization

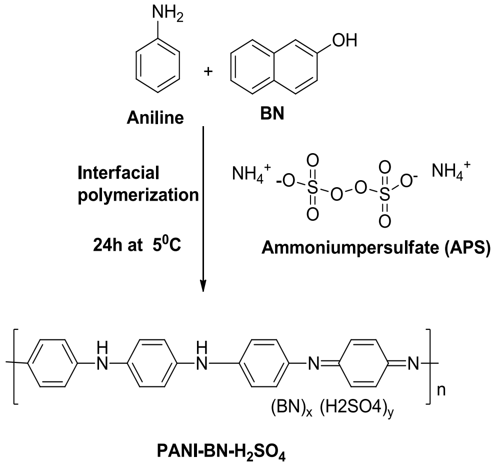
FT-IR spectra of powder samples were registered on a GC-FT-IR spectrometer 670 Nicolet Nexus (Minnesota, USA) using the KBr pellet technique. XRD profiles for the powders were obtained on a Bruker AXS D8 advance X-ray diffractometer (Karlsruhe, Germany) with CuK$_{\alpha}$ radiation (land continuous) ($\lambda$=1.54 Å) at a scan speed of $0.045^{\circ}$min$^{-1}$. Morphological characterizations were performed using Hitachi S3400 scanning electron microscope (Tokyo, Japan). The powder sample was mounted on a double-sided adhesive carbon disk and sputter-coated with a thin layer of gold (500Å) to prevent sample from possible charging. Transmission electron microscopy (TEM) measurement was carried out with Hitachi S-5500 instrument operated at an accelerate voltage of 30 kV. UV-Vis spectra were measured using a Shimadzu model 1700 spectrophotometer. Fluorescence spectra were recorded on a Spex model Fluoromax-3 spectrofluorometer. Confocal Micro Raman spectra were recorded using a Horiba Jobin-Yvon LabRam HR spectrometer with a 17 mW internal He-Ne (Helium-Neon) laser source of excitation wavelength 632.8 nm. Thermo gravimetric analysis was performed using a TA Instruments Q500 Thermo gravimetric Analyzer (New Castle, USA) for powder samples at a heating rate of 10 °C min$^{-1}$ from ambient temperature to 700 ºC under nitrogen atmosphere. Cyclic voltammetric experiment was performed using CHI620C electrochemical analyser with three electrode system of platinum as working electrode, calomel as reference electrode, platinum as counter electrode with the electrolyte of polymer sample in 0.1 M tetrabutylammonium perchlorate of dimethyl sulfoxide solution. Electrochemical experiment was carried at ambient temperature at a scan rate of 100 mV s$^{-1}$ in the potential window of -1.5 to 1.5 V.

## 3. Results and discussion

### 3.1 Physical and electrical properties of Polyaniline-sulfate salts

Aniline in chloroform solvent with or without β-naphthol (BN) was oxidized using aqueous solution of ammonium persulfate oxidant. Aqueous solution of oxidant was added slowly through the wall of the beaker to the chloroform solution. After the addition of oxidant, the mixture was kept at 5 °C without stirring the reaction mixture. The reaction was continued for 24 h. and green colour product of polyaniline was formed (Scheme-1). The values of yield, density, conductivity and elemental composition of PANI salts are reported in Table 1. Elemental analysis result shows the presence of sulfur element (Approx.5%) and this result signpost that the presence of sulfuric acid as dopant on polyaniline salt. Sulfuric acid was generated during the oxidation of aniline by ammonium persulfate and doped on to PANI. Yield of the PANI-$H_2SO_4$ prepared without BN was 0.7 g with a pellet conductivity of 0.1 S cm$^{-1}$. Conductivity of this PANI-$H_2SO_4$ is lower than that of the conventional polyaniline salts prepared in presence of acid, which are in the range of 2.7 to 6.1 S cm$^{-1}$.[23] This observation indicates that use of acid increases the oxidizing power of ammonium persulfate and doping amount on PANI. In order to increase the conductivity of PANI-$H_2SO_4$ (0.1 S cm$^{-1}$), we used an alcohol, β-naphthol, in the reaction instead of using toxic acids. The values of yield and conductivity increases with increasing the amount of BN, attains a maximum and then decreases. Value of conductivity of PANI-$H_2SO_4$ was increased from 0.1 to 1.2 Scm$^{-1}$ for PANI-BN1-$H_2SO_4$. This result indicates that the use of BN increase the conductivity of PANI-$H_2SO_4$. The important achievement in this work is the use of alcohol instead of toxic acid in the formation of PANI salt with comparable yield, density and conductivity of the conventional polyaniline salts.

Spectral, thermal, morphological, optoelectronic and fluorescent properties of PANI-$H_2SO_4$ is compared with that of PANI-$H_2SO_4$ prepared with BN are the results are discussed here.



**Scheme-1** Synthesis of polyaniline salt, PANI-BN-$H_2SO_4$.

**Table 1** Yield ,Conductivity , Density and Elemental analysis Results for PANI-$H_2SO_4$ and Various PANI-BN-$H_2SO_4$ salts

| System | Yield (g) | Conductivity (S $cm^{-1}$ ) | Density (g $cm^{-3}$) | C (%) | H (%) | N (%) | S (%) |
|---|---|---|---|---|---|---|---|
| PANI-BN0.5-$H_2SO_4$ | 0.8 | 0.6 | 1.37 | 9.8 | 52.9 | 4.6 | 5.0 |
| PANI-BN1-$H_2SO_4$ | 1.0 | 1.2 | 1.37 | 10.0 | 52.6 | 4.6 | 5.4 |
| PANI-BN2-$H_2SO_4$ | 1.0 | 0.8 | 1.34 | 10.0 | 52.4 | 4.5 | 5.9 |
| PANI-BN4-$H_2SO_4$ | 0.7 | 0.4 | 1.34 | 9.9 | 54.0 | 4.5 | 5.0 |
| PANI-$H_2SO_4$ | 0.7 | 0.1 | 1.36 | 10.9 | 54.6 | 4.1 | 4.0 |

### 3.2 Spectral Properties

Fourier transform infrared spectra of BN, PANI-BN1-$H_2SO_4$, PANI-$H_2SO_4$ are shown in( Fig. 1). The major peaks observed for PANI-BN1-$H_2SO_4$ and PANI-$H_2SO_4$ are given in Table 2. Major peaks observed for both PANI-BN1-$H_2SO_4$, and PANI-$H_2SO_4$ systems indicate the formation of polyaniline in salt form.[24] However, shift in the peak positions for C=C str. of quinonoid and N=Q=N vibration were observed. This is due to the difference in the efficiency of undergoing oxidation of aniline and doping on polyaniline system. This result is in accordance with the difference in conductivity for PANI-BN1-$H_2SO_4$ and PANI-$H_2SO_4$. In the PANI-BN1-$H_2SO_4$, peaks due to BN (Fig.1a) are not observed.

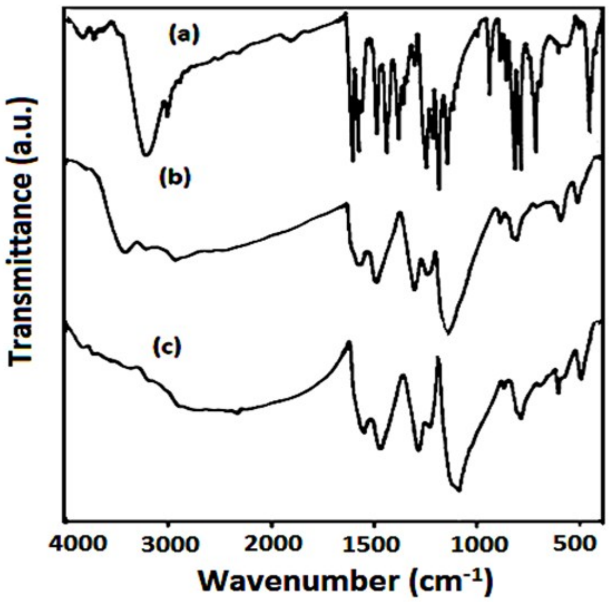


**Fig. 1** Infrared spectra of (a) BN (b) PANI-BN1-$H_2SO_4$ and (c) PANI-$H_2SO_4$.

**Table 2** IR Spectral Assignments for PANI Salts

| Assignment | PANI-BN1- $H_2SO_4$ ($cm^{-1}$) | PANI-$H_2SO_4$ ($cm^{-1}$) |
|---|---|---|
| C=C str., quinonoid ring | 1567 | 1559 |
| C=C str., benzenoid ring | 1484 | 1482 |
| C-N str., quinonoid ring | 1304 | 1300 |
| C-N str., benzenoid ring | 1240 | 1252 |
| N=Q=N vibration, where Q is the quionoid ring | 1145 | 1105 |
| C-H out-of-plane bending For a 1,4-substituted Benzene | 882 | 880 |
| 1,4 disubstitutedbenzene | 802 | 799 |

Raman spectra of PANI-$H_2SO_4$ and PANI-BN1-$H_2SO_4$ are shown in (Fig. 2). Major peaks observed for PANI-$H_2SO_4$ are assigned to 3150 (N-H str.), 1260 (benzenoid, C-N str.), 1115 (C-H bending) and 615 $cm^{-1}$(aromatic ring deformation). In the case of PANI-BN1-$H_2SO_4$, the major peaks are assigned to 3260 $cm^{-1}$ (N-H str.), 1580 (quinonoid ring, C=C str.), 1425 (quinonoid ring, C-C str.), 1360 (quinonod ring, C-N str.) and 615 $cm^{-1}$ (aromatic ring deformation). Raman spectra support the formation of polyaniline salt.

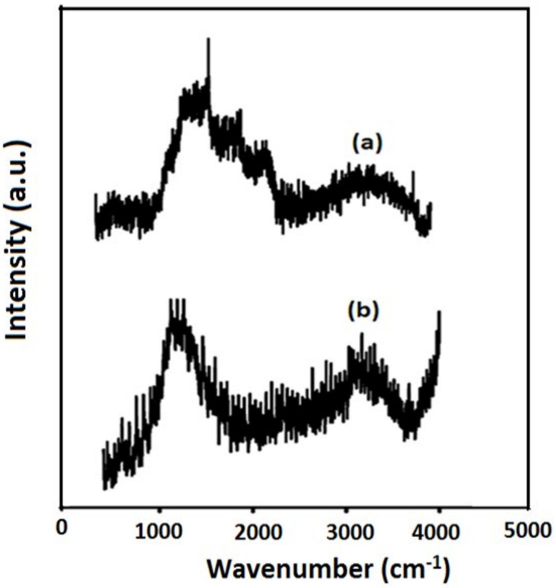


**Fig. 2** Raman spectra of (a) PANI-BN1-$H_2SO_4$ and (b) PANI-$H_2SO_4$.

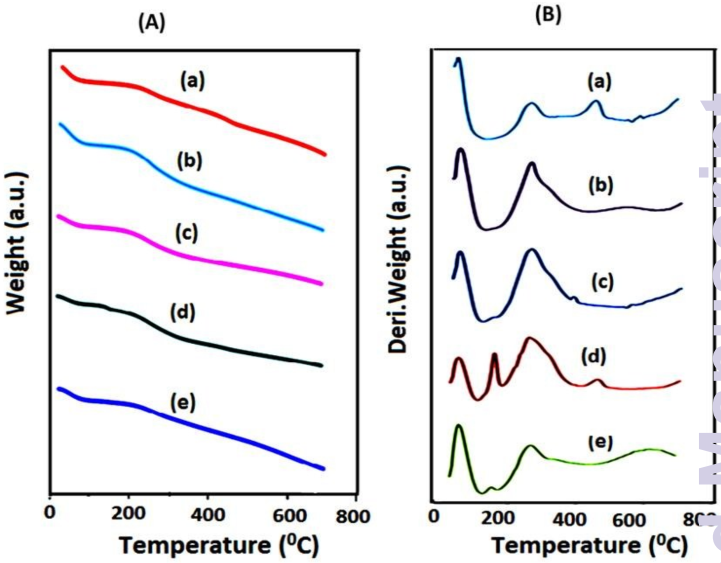


**Fig. 3** (A) TG and(B) DTG thermograms of (a) PANI-$H_2SO_4$, (b) PANI-BN0.5-$H_2SO_4$, (c) PANI-BN1-$H_2SO_4$, (d) PANI-BN2-$H_2SO_4$, and (e) PANI-BN4-$H_2SO_4$.

### 3.3 Thermal behaviour

Thermal behaviour of PANI-$H_2SO_4$ salts prepared with and without use of BN was carried out from thermal analysis. TG and DTG thermograms of PANI-$H_2SO_4$ and PANI-BN1-$H_2SO_4$ salts are given in (Fig. 3). DTG thermograms of PANI-$H_2SO_4$ prepared with various amounts of BN show three steps weight loss behaviour and however, the salt prepared without BN show two steps weight loss behaviour i.e. 1st and 3rd peak maxima in comparison with the salts prepared with BN (Fig. 3B). DTG peak maximum temperature, peak end temperature and the weight loss amount are reported in (Table 3). First peak in the DTG thermograms is due to the presence of moisture on PANI salt. The second peak is due to the escape of BN from the polymer chain. Third peak is due to the escape of sulphuric acid along with BN. Third peak maxima and third peak end temperatures are very nearly the same for all the PANI-$H_2SO_4$ salts. This result indicates that temperature at around 300 °C, both the dopants (BN and $H_2SO_4$) escapes from the polymer chain and after 300 °C, polymer undergoes degradation.

### 3.4 Morphology

Field emission scanning electron microscopic images of PANI-$H_2SO_4$ and PANI-BN-$H_2SO_4$ salts synthesized by various amounts of BN are given in (Fig. 4). SEM image of PANI-$H_2SO_4$ shows nano fiber morphology with thorns on the edge of the fiber surface with uniform pours. SEM images of PANI-BN-$H_2SO_4$ salts also show nano fiber morphology with thorns on the edge of the fiber surface and the fibers are coming closer to each other with increasing amounts of BN. Energy Dispersive X-ray Analysis of PANI-BN1-$H_2SO_4$ shows the presence of sulphur element and this result support the presence of 5.4 wt.% of sulphur element from elemental analysis result (Table 1).

TEM image of PANI-BN1-$H_2SO_4$ is shown in (Fig. 5). It shows bundles of fiber in the low magnification. In order to find out the size of the fiber, the image was taken in higher magnitude which clearly shows nano fiber morphology with a width of 25-80 nm. TEM image supports the SEM image of PANI-BN1-$H_2SO_4$.

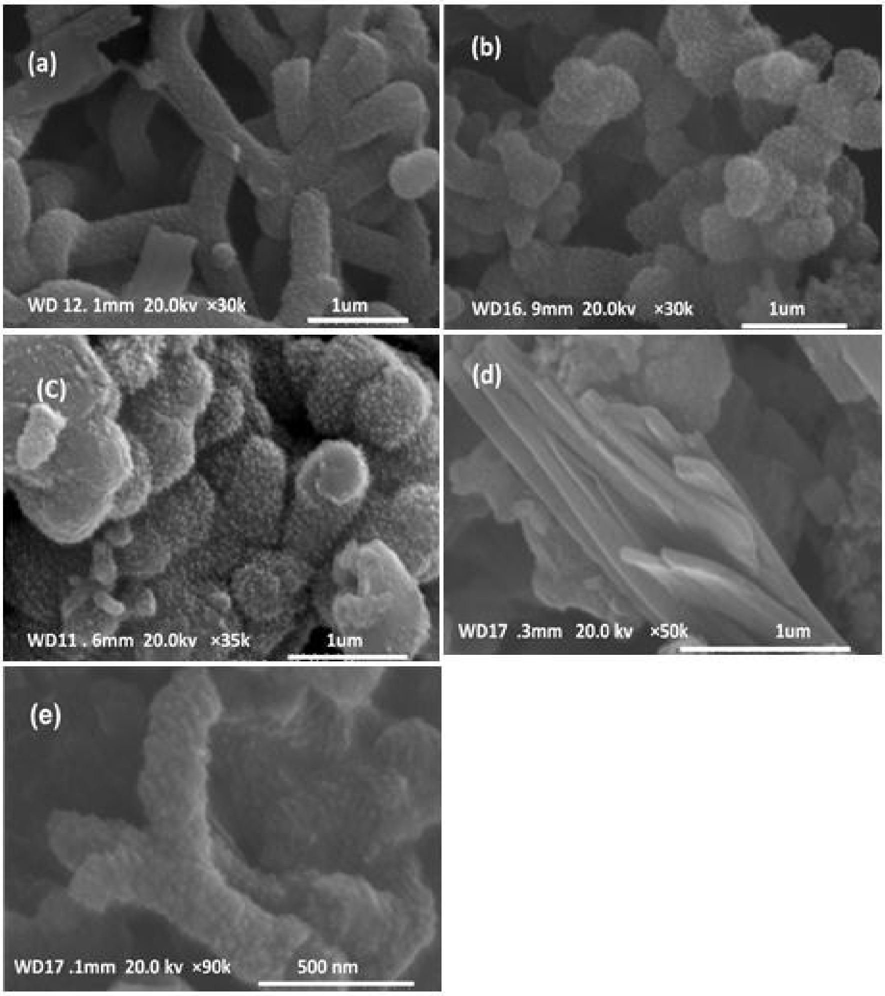


**Fig.** 4 FE-SEM images of (a) PANI-$H_2SO_4$, (b) PANI-BN0.5-$H_2SO_4$, (c) PANI-BN1-$H_2SO_4$, (d) PANI-BN2-$H_2SO_4$, and (e) PANI-BN4-$H_2SO_4$.

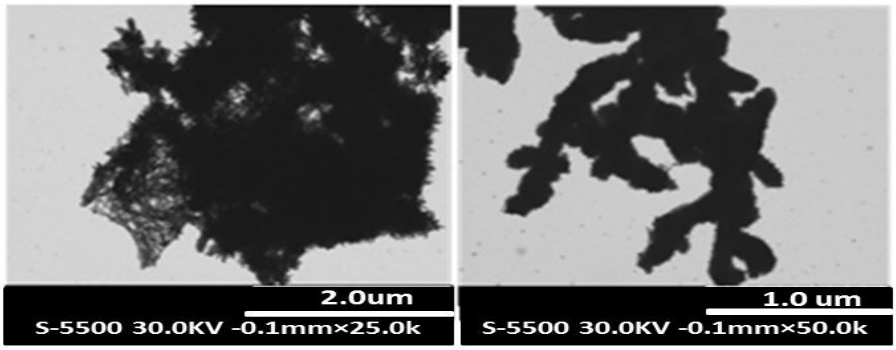


**Fig. 5** TEM image of PANI-BN1-$H_2SO_4$ (a) low and (b) high magnification.

**Table 3** TG and DTG results for PANI- $H_2SO_4$ salts

| System | 1st peak end (°C) | 2nd peak end (°C) | 3rd peak end (°C) | 1st step weight loss (wt.%) | 2nd step weight loss (wt.%) | 3rd step weight loss (wt.%) | 1st peak max (°C) | 2nd peak max (°C) | 3rd peak max (°C) |
|---|---|---|---|---|---|---|---|---|---|
| PANI- $H_2SO_4$ | 100 | 160 | 308 | 5.5 | 0.1 | 6.2 | 48 | Nil | 250 |
| PANI-BN0.5-$H_2SO_4$ | 111 | 156 | 290 | 7.8 | 0.5 | 10.2 | 50 | 126 | 255 |
| PANI-BN1-$H_2SO_4$ | 108 | 160 | 304 | 6.5 | 1.0 | 13.2 | 48 | 133 | 248 |
| PANI-BN2-$H_2SO_4$ | 108 | 172 | 305 | 5.2 | 3.6 | 13.7 | 49 | 156 | 255 |
| PANI-BN4-$H_2SO_4$ | 103 | 153 | 310 | 7.0 | 1.1 | 10.4 | 51 | 143 | 255 |

1st step weight loss = weight loss up to first peak end = Moisture loss
2nd step weight loss = weight loss between 1st and 2nd peak end = BN loss
3rd step weight low = weight loss between 2nd and 3rd peak end – sulfuric acid loss (approximately

### 3.5 Crystalline nature

To find out the crystalline nature, x-ray diffraction patters were recorded for BN, PANI-BN1-$H_2SO_4$ and PANI-$H_2SO_4$ and are shown in (Fig. 6). The d-spacing of the peaks observed are given in Table 4. XRD spectrum of PANI-$H_2SO_4$ showed two broad peaks indicates amorphous nature. The XRD pattern of PANI-BN1-$H_2SO_4$ showed many sharp peaks compared to amorphous PANI-$H_2SO_4$ indicating high crystalline nature. XRD spectrum of BN showed many sharp crystalline peaks and on comparison of the XRD peaks of BN with PANI-BN1-$H_2SO_4$, some of the BN peaks are observed in PANI-BN1-$H_2SO_4$. This result signposts that PANI-BN1-$H_2SO_4$ may contains BN.

**Table 4** XRD d-Spacing Values for PANI Salts.

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| a | 16.2 (s) | --- | 8.0 (i) | 5.9 (s) | 5.3 (s) | 4.6 (i) | --- | --- | 4.3 (s) | 4.1 (i) | 3.7 (m) | 3.5 (i) | 3.3 (m) | 3.1 (m) | 2.9 (s) | 2.8 (s) |
| b | --- | 14.7 (i) | --- (s) | --- (s) | 5.3 (s) | --- | 4.9 (m) | 4.4 (i) | --- | 4.2 (m) | 3.7 (m) | 3.5 (m) | --- | 3.1 (s) | 2.9 (s) | 2.8 (s) |
| c | | | | | | | | | | | | 3.5 (i) | | | | |

(a) BN (b) PANI-BN1-$H_2SO_4$ and (c) PANI-$H_2SO_4$, i - intense, m – medium, s - small peak

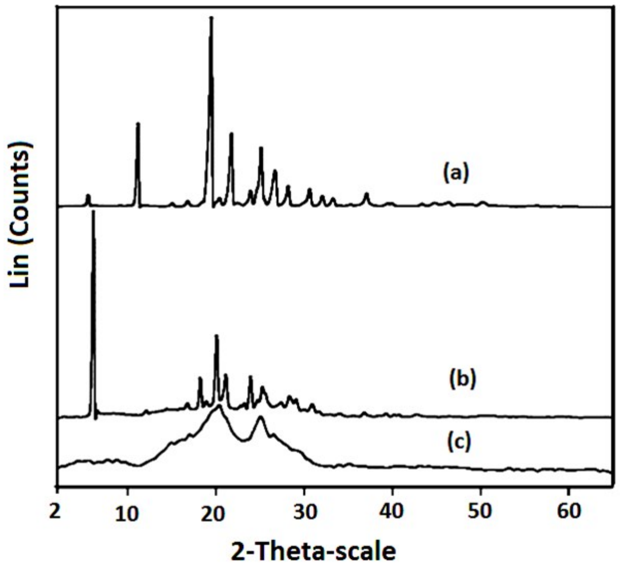


**Fig. 6** X-ray diffraction patterns of (a) BN (b) PANI-BN1-$H_2SO_4$ and (c) PANI-$H_2SO_4$.

### 3.6 Optoelectronic properties

Electronic absorption spectrum of polyaniline base[25] shows two distinct absorption bands located between 315–345 and 590–650 nm depending on the method of preparation and/or processing of polyaniline. The bands around 315–345, and 590–650nm were assigned to the excitation of the amine and imine segment of the polyaniline chain respectively. In the case of fully protonated polyaniline in salt form, the peak around 590–650nm disappears and a new peak above 725 nm appear in addition to the appearance of peak around 325-360 nm. The peak around 325-360 nm corresponds to π to π* transition and the peak (400-430 nm) corresponds to polaron to π* transition. The new peak above 725 nm corresponds to the π to localized polaron band.[26]

UV-vis absorption spectroscopic method was employed to investigate the changes in optical properties of PANI-$H_2SO_4$ and PANI-$H_2SO_4$ containing β-naphthol. Electronic absorption spectra of BN, PANI-BN1-$H_2SO_4$, PANI-$H_2SO_4$ at ambient temperature in dimethyl sulfoxide solvent are shown in (Fig. 7). Spectrum of BN showed a peak at 336 nm due to π to π* transition. Absorption spectrum of PANI-BN1-$H_2SO_4$ showed two broad peaks at around 400 and 803 nm. However, absorption spectrum of PANI-$H_2SO_4$ showed two broad peaks at around 335 and 580 nm with a shoulder peak around 365 nm. Both the polyaniline salts, PANI-BN-$H_2SO_4$ and PANI-$H_2SO_4$ indicate the formation of polyaniline in salt formation. However, the absence of a peak above 725 nm in the case of PANI-$H_2SO_4$ signposts less conjugation, which is the reason for lower conductivity.

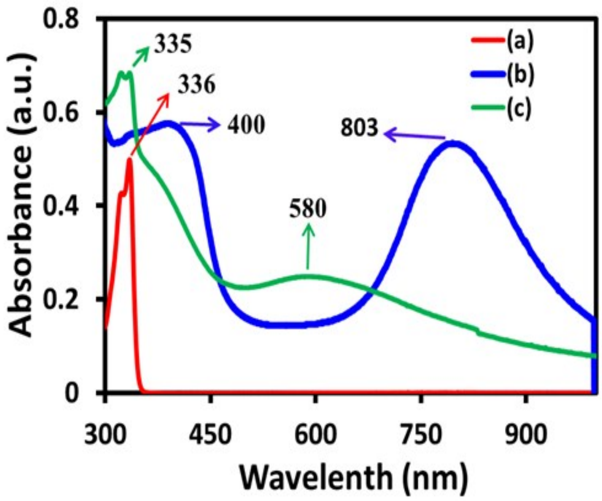


**Fig. 7** Uv-Vis spectra of (a) BN (b) PANI-BN1-$H_2SO_4$ and (c) PANI-$H_2SO_4$.

The fluorescence emission measurements were carried out in dimethyl sulfoxide at ambient temperature (Fig. 8). Upon excitation at 325 nm BN solution in DMSO shows a fluorescence band at 370 nm. The fluorescence emission spectrum of PANI-$H_2SO_4$ exhibits emission band at 358 nm. The emission spectrum of PANI-$H_2SO_4$ containing BN shows peaks at 440 and 460 along with shoulder peaks at 415 nm. Thus appearance of new emission peak clearly indicates doping of PANI-$H_2SO_4$ with BN is perfect one and the BN as well as PANI-$H_2SO_4$ are not in free form.

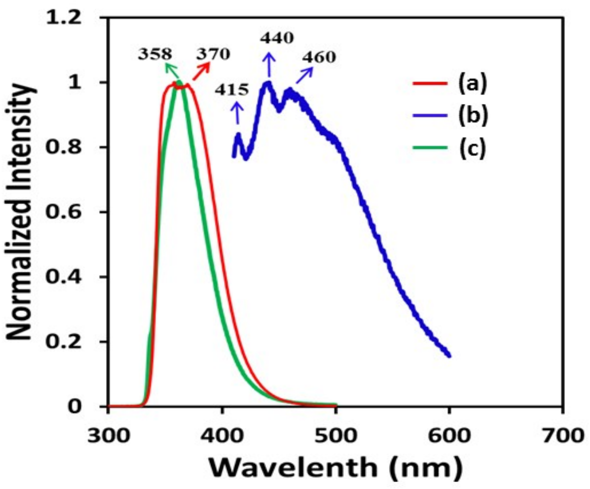


**Fig. 8** Fluorescence spectra of (a) BN (b) PANI-BN-$H_2SO_4$ and (c) PANI-$H_2SO_4$.

For reversible redox reactions, cyclic voltammetry can give a direct measure of the HOMO and LUMO levels. Cyclic voltammetric experiments were performed for PANI-BN1-$H_2SO_4$ and PANI-$H_2SO_4$ in the supporting electrolyte of 0.1M tetrabutylammonium perchlorate in dimethyl sulfoxide (Fig. 9). The energy levels of the HOMO and LUMO were calculated using the following equations

.

$$E\,(\mathrm{HOMO}) = -e\,[E_{ox}\ \mathrm{onset} + 4.4] \quad (1)$$

$$E\,(\mathrm{LUMO}) = -e\,[E_{red}\ \mathrm{onset} + 4.4] \quad (2)$$

CV of PANI-BN1-$H_2SO_4$ showed E onset oxidation and reduction potentials at 0.91 and -0.55 V respectively. Band gap energy was calculated from the above equation as 1.46 eV which is very close to that of the energy gap found from absorption spectrum (1.54 eV). However, only oxidation potential at 0.92 V was observed for PANI-$H_2SO_4$ system (Fig. 9).

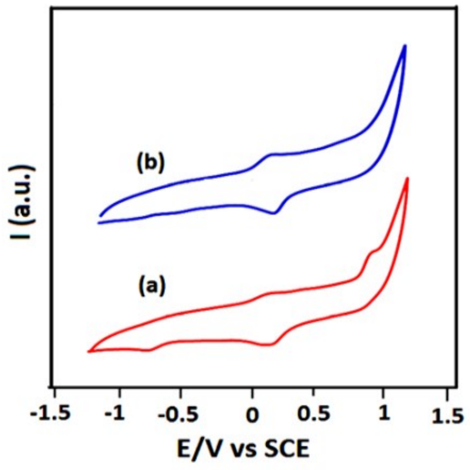


**Fig. 9** CV of (a) PANI-$H_2SO_4$ (b) PANI-BN1-$H_2SO_4$.

Oxidation of aniline by ammonium persulfate with β-naphthol gives polyaniline salt containing dual dopants of β-naphthol and sulfuric acid group (Scheme 1). Generally, alcohol forms hydrogen bond with ammine acceptor.[27] In the polyaniline salt, β-naphthol having hydrogen atom is involved through hydrogen bonding with the nitrogen atom of polyaniline and sulfuric acid group was generated from ammonium persulfate during the polymerization of aniline and get doped on polyaniline. This polyaniline salt can be tried out in various applications such as energy storage devices, sensor, light-emitting diodes, solar cell, microelectronics, etc.

## 4. Conclusions

In summary, polyaniline salt was synthesized without using any acids in the polymerization reaction. Polyaniline salt containing dual dopants of β-naphthol and sulfuric acid was obtained with high yield and conductivity (1.2 S $cm^{-1}$) comparable with that of the conventional polyaniline salts prepared using acids. Higher conductivity value of polyaniline salts containing dual dopants compared to that of polyaniline-sulfate salt is accounted to higher conjugation and this was concluded from FT-IR, UV-Vis, fluorescent, CV studies. This novel polyaniline-β-naphthol-sulfuric acid salt was obtained in 25-80 nm width of fiber bundles with thorns at the edge of the fibers. In addition, polyaniline salt showed high crystalline nature compared to that of the conventional polyaniline of semicrystalline nature. Moreover, this polyaniline shows broad fluorescence spectrum around 450 nm.

## Acknowledgements

We thank the Department of Science & Technology, New Delhi for funding under the project (DST/TSG/PT/2011/179-G). We also thank, Dr. Vijayamohanan K Pillai, Director, CSIR-CECRI for his valuable discussions and Dr. L. Giribabu, Senior scientist, IICT for his help in recording fluorescence spectra.

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# A novel process of alcohol promoted polymerization of aniline to form nano fibrous, fluorescent and highly crystalline polyaniline salt

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***New J. Chem.***,
**DOI:**
**First published online :**

Use of acid was replaced by alcohol in the polymerization of aniline to highly crystalline, nanofibrous, fluorescent and conducting polyaniline salt.