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A novel process of alcohol promoted polymerization of aniline to form a nanofibrous, fluorescent and highly crystalline polyaniline salt

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

1. Introduction

Polyaniline belongs to the conjugated class of organic conducting polymers. Among conducting polymers, polyaniline (PANI) has attracted much attention because of its properties like ease of synthesis from easily available monomers, controllable electrical conductivity, simplicity in doping and de-doping, chemical stability, good environmental stability, mechanical flexibility, low cost, and has various applications. Applications of polyaniline such as sensors,¹ electrochromic 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 and catalysts¹² have been covered in a review by Gordana Ćirić-Marjanovic¹³ (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

The fluorescence properties of a few polyaniline systems have been reported in the literature such as polyaniline–fluorescein,¹⁶ polyaniline–perylene-tetracarboxylic acid,¹⁷ polyaniline base prepared from polyaniline–hydrochloride salt¹⁸ and polyaniline–*meso*-tetrakis(4-sulfonato phenyl) porphyrin.¹⁹

The conductivity of polyaniline salts depends on their 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 basic form of PANI, emeraldine base (EB), is 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 of acid. Aniline has been oxidized by ammonium persulfate to PANI-H₂SO₄ with and without using H₂SO₄.^{21,22} The conductivity of PANI-H₂SO₄ prepared without using acid is lower than that of the salt prepared using sulfuric acid.²¹ This is due to an increase in the 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 highly crystalline, nanofibrous morphology with fluorescence 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 persulfate and sulfuric acid (Rankem India) were used as received. Distilled water was used for all the reactions.

2.2 Synthesis of polyaniline- β -naphthol-sulfate

In a typical synthesis, 1 ml of aniline (11 mmol) and β -naphthol (0.5, 1, 2, 4 mmol) were dissolved in 15 ml of chloroform.

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A freshly prepared solution of 2.8 g of ammonium persulfate (12.3 mmol) in 30 ml of water was added dropwise into the organic solution through the side of the beaker at ambient temperature. The reaction was continued under 5 °C in a refrigerator for 24 h. The obtained deep-green product was filtered, washed with ample amounts of water and acetone. The sample was dried at 50 °C until a constant weight. In this work, these samples are designated as PANI-BN0.5-H₂SO₄, PANI-BN1-H₂SO₄, PANI-BN2-H₂SO₄ and PANI-BN4-H₂SO₄.

Polyaniline-sulfate salt (PANI-H₂SO₄) was prepared by the above procedure without the use of β-naphthol.

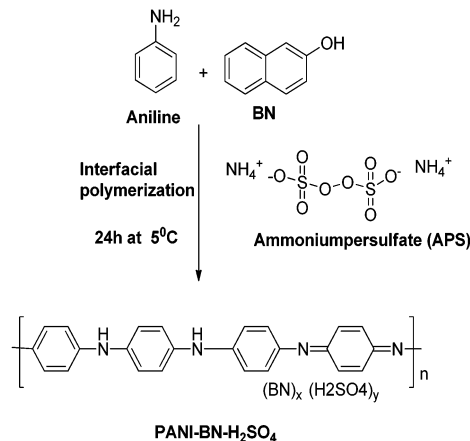
2.3 Characterization

The FT-IR spectra of powder samples were recorded 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 (Karlruhe, Germany) with CuK_α radiation (λ = 1.54 Å) at a scan speed of 0.045° min⁻¹. Morphological characterizations were performed using a 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 (500 Å) to prevent the sample from possible charging. Transmission electron microscopy (TEM) measurements were carried out using a Hitachi S-5500 instrument operated at an accelerating voltage of 30 kV. UV-Vis spectra were recorded 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 an excitation wavelength of 632.8 nm. Thermogravimetric analysis was performed using a TA Instruments Q500 Thermogravimetric Analyzer (New Castle, USA) for powder samples at a heating rate of 10 °C min⁻¹ from ambient temperature to 700 °C under a nitrogen atmosphere. Cyclic voltammetric experiments were performed using a CHI620C electrochemical analyser with a three electrode system comprising platinum as the working electrode, calomel as the reference electrode, and platinum as the counter electrode with the electrolyte of the polymer sample in 0.1 M tetrabutylammonium perchlorate of dimethyl sulfoxide solution. Electrochemical experiments were carried out 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 an aqueous solution of the ammonium persulfate oxidant. The aqueous solution of the oxidant was added slowly through the wall of the beaker to the chloroform solution. After the addition of the oxidant, the mixture was maintained at 5 °C without stirring the reaction mixture. The reaction was continued for 24 h and a green coloured product of polyaniline was formed (Scheme 1).



Scheme 1 Synthesis of polyaniline salt, PANI-BN-H₂SO₄.

The values of yield, density, conductivity and elemental composition of PANI salts are reported in Table 1. Elemental analysis results show the presence of sulfur element (Approx. 5%) and these results indicate the presence of sulfuric acid as a dopant on polyaniline salt. Sulfuric acid was generated during the oxidation of aniline by ammonium persulfate and doped onto PANI. The yield of PANI-H₂SO₄ prepared without BN was 0.7 g with a pellet conductivity of 0.1 S cm⁻¹. The conductivity of this PANI-H₂SO₄ is lower than that of the conventional polyaniline salts prepared in the presence of acid, which are in the range of 2.7 to 6.1 S cm⁻¹.²³ This observation indicates that the use of acid increases the oxidizing power of ammonium persulfate and the doping amount on PANI. In order to increase the conductivity of PANI-H₂SO₄ (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 increase upon increasing the amount of BN, attain a maximum and then decrease. The value of conductivity of PANI-H₂SO₄ was increased from 0.1 to 1.2 S cm⁻¹ for PANI-BN1-H₂SO₄. This result indicates that the use of BN increases the conductivity of PANI-H₂SO₄. An 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.

The spectral, thermal, morphological, optoelectronic and fluorescence properties of PANI-H₂SO₄ are compared with those of PANI-H₂SO₄ prepared using BN and the results are discussed here.

3.2 Spectral properties

The Fourier transform infrared spectra of BN, PANI-BN1-H₂SO₄, and PANI-H₂SO₄ are shown in Fig. 1. The major peaks observed

Table 1 Yield, conductivity, density and elemental analysis results for PANI-H₂SO₄ and various PANI-BN-H₂SO₄ salts

System	Yield (g)	Conductivity (S cm ⁻¹)	Density (g cm ⁻³)	C (%)	H (%)	N (%)	S (%)
PANI-BN0.5-H ₂ SO ₄	0.8	0.6	1.37	9.8	52.9	4.6	5.0
PANI-BN1-H ₂ SO ₄	1.0	1.2	1.37	10.0	52.6	4.6	5.4
PANI-BN2-H ₂ SO ₄	1.0	0.8	1.34	10.0	52.4	4.5	5.9
PANI-BN4-H ₂ SO ₄	0.7	0.4	1.34	9.9	54.0	4.5	5.0
PANI-H ₂ SO ₄	0.7	0.1	1.36	10.9	54.6	4.1	4.0

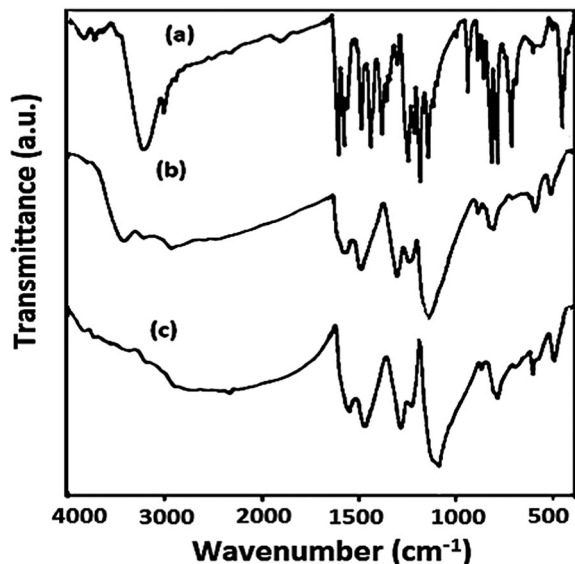


Fig. 1 Infrared spectra of (a) BN (b) PANI-BN1-H₂SO₄ and (c) PANI-H₂SO₄.

for PANI-BN1-H₂SO₄ and PANI-H₂SO₄ are given in Table 2. Major peaks observed for both PANI-BN1-H₂SO₄ and PANI-H₂SO₄ systems indicate the formation of polyaniline in salt form.²⁴ However, a shift in the peak positions for C=C str. of quinonoid and N=Q=N vibration was observed. This is due to the difference in the efficiency of the undergoing oxidation of aniline and doping on the polyaniline system. This result is in accordance with the difference in conductivity for PANI-BN1-H₂SO₄ and PANI-H₂SO₄. In PANI-BN1-H₂SO₄, peaks due to BN (Fig. 1a) are not observed.

The Raman spectra of PANI-H₂SO₄ and PANI-BN1-H₂SO₄ are shown in Fig. 2. Major peaks observed for PANI-H₂SO₄ 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-H₂SO₄, 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 (quinonoid ring, C-N str.) and 615 cm⁻¹ (aromatic ring deformation). Raman spectra support the formation of polyaniline salt.

3.3 Thermal behaviour

Thermal behaviour of PANI-H₂SO₄ salts prepared with and without the use of BN was obtained from thermal analysis.

Table 2 IR spectral assignments for PANI salts

Assignment	PANI-BN1-H ₂ SO ₄ (cm ⁻¹)	PANI-H ₂ SO 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 quinonoid ring	1145	1105
C-H out-of-plane bending for a 1,4-substituted benzene	882	880
1,4-Disubstitutedbenzene	802	799

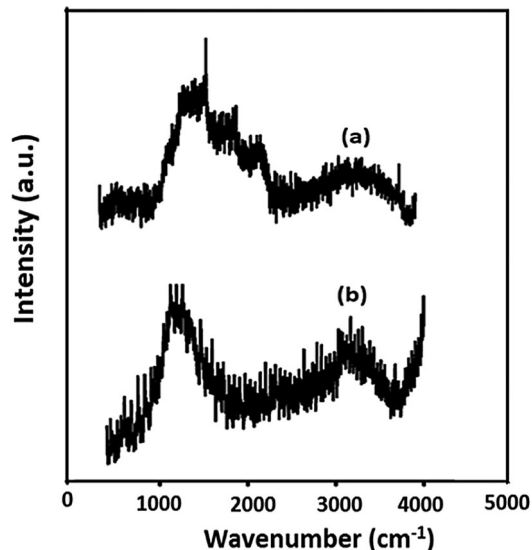


Fig. 2 Raman spectra of (a) PANI-BN1-H₂SO₄ and (b) PANI-H₂SO₄.

TG and DTG thermograms of PANI-H₂SO₄ and PANI-BN1-H₂SO₄ salts are given in Fig. 3. DTG thermograms of PANI-H₂SO₄ prepared using various amounts of BN show three step weight loss behaviour and, however, the salt prepared without BN shows two step weight loss behaviour *i.e.* 1st and 3rd peak maxima in comparison with the salts prepared using BN (Fig. 3B). The DTG peak maximum temperature, peak end temperature and the weight loss amount are reported in Table 3. The first peak in the DTG thermogram is due to the presence of moisture on PANI salt. The second peak is due to the escape of BN from the polymer chain. The 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-H₂SO₄ salts. This result indicates that at around 300 °C, both the dopants (BN and H₂SO₄) escape from

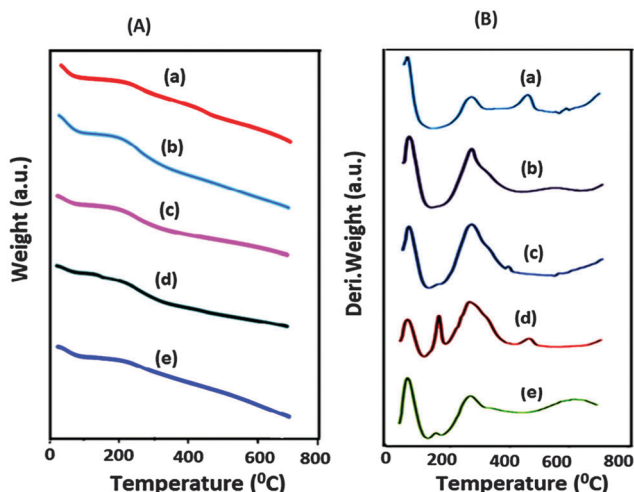


Fig. 3 (A) TG and (B) DTG thermograms of (a) PANI-H₂SO₄, (b) PANI-BN0.5-H₂SO₄, (c) PANI-BN1-H₂SO₄, (d) PANI-BN2-H₂SO₄, and (e) PANI-BN4-H₂SO₄.

Table 3 TG and DTG results for PANI-H₂SO₄ salts^a

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 ₂ SO ₄	100	160	308	5.5	0.1	6.2	48	Nil	250
PANI-BN0.5-H ₂ SO ₄	111	156	290	7.8	0.5	10.2	50	126	255
PANI-BN1-H ₂ SO ₄	108	160	304	6.5	1.0	13.2	48	133	248
PANI-BN2-H ₂ SO ₄	108	172	305	5.2	3.6	13.7	49	156	255
PANI-BN4-H ₂ SO ₄	103	153	310	7.0	1.1	10.4	51	143	255

^a 1st step weight loss = weight loss up to the first peak end = moisture loss. 2nd step weight loss = weight loss between 1st and 2nd peak ends = BN loss. 3rd step weight loss = weight loss between 2nd and 3rd peak ends – sulfuric acid loss (approximately).

the polymer chain and after 300 °C, the polymer undergoes degradation.

3.4 Morphology

Field emission scanning electron microscopic images of PANI-H₂SO₄ and PANI-BN-H₂SO₄ salts synthesized using various amounts of BN are given in Fig. 4. The SEM image of PANI-H₂SO₄ shows nanofiber morphology with thorns at the edge of the fiber surface with uniform pores. The SEM images of PANI-BN-H₂SO₄ salts also show nanofiber morphology with thorns at 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-H₂SO₄ shows the presence of sulphur element and this result supports the presence of 5.4 wt% of sulphur element from elemental analysis results (Table 1).

The TEM image of PANI-BN1-H₂SO₄ is shown in Fig. 5. It shows bundles of fibers at low magnification. In order to find out the size of the fiber, the image was obtained at higher magnification, which clearly shows nanofiber morphology with a width of 25–80 nm. The TEM image supports the SEM image of PANI-BN1-H₂SO₄.

3.5 Crystalline nature

To find out the crystalline nature, X-ray diffraction patterns were recorded for BN, PANI-BN1-H₂SO₄ and PANI-H₂SO₄ and

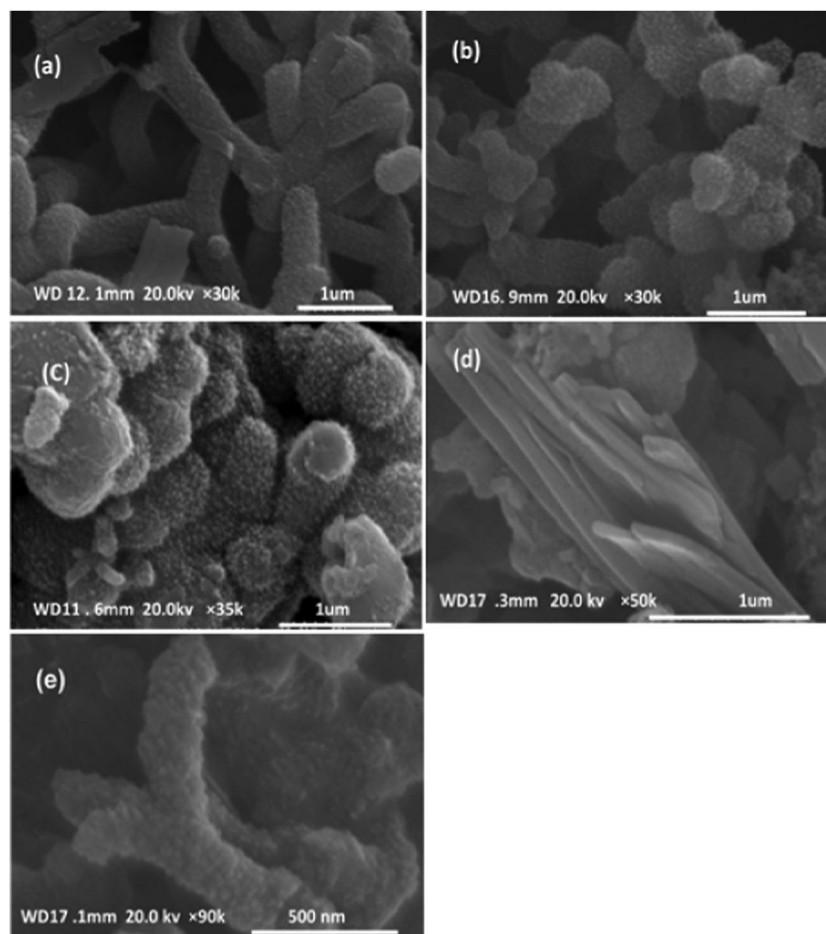


Fig. 4 FE-SEM images of (a) PANI-H₂SO₄, (b) PANI-BN0.5-H₂SO₄, (c) PANI-BN1-H₂SO₄, (d) PANI-BN2-H₂SO₄, and (e) PANI-BN4-H₂SO₄.

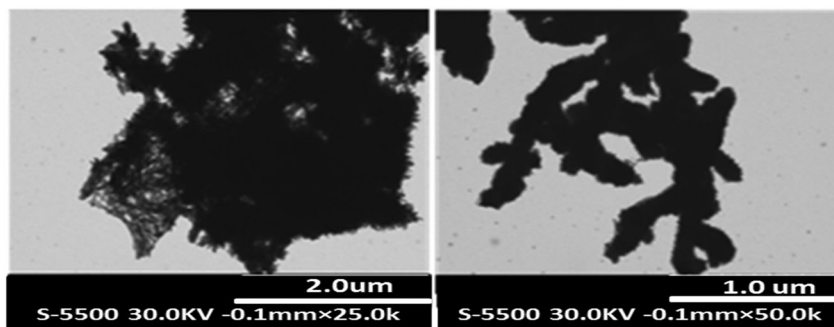


Fig. 5 TEM image of PANI-BN1-H₂SO₄ at (a) low and (b) high magnification.

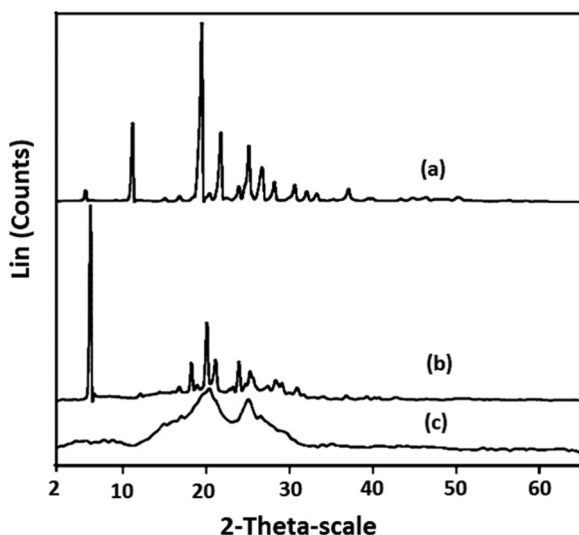


Fig. 6 X-ray diffraction patterns of (a) BN (b) PANI-BN1-H₂SO₄ and (c) PANI-H₂SO₄.

are shown in Fig. 6. The *d*-spacing of the observed peaks is given in Table 4. The XRD spectrum of PANI-H₂SO₄ showed two broad peaks indicating its amorphous nature. The XRD pattern of PANI-BN1-H₂SO₄ showed many sharp peaks compared to amorphous PANI-H₂SO₄ indicating its highly crystalline nature. The XRD pattern of BN showed many sharp crystalline peaks and comparison of the XRD peaks of BN with PANI-BN1-H₂SO₄ showed that some BN peaks are observed in PANI-BN1-H₂SO₄. These results indicate that PANI-BN1-H₂SO₄ may contain BN.

3.6 Optoelectronic properties

The electronic absorption spectrum of polyaniline base²⁵ 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 at around 315–345 and 590–650 nm were assigned to the excitation of the amine and imine segments of the polyaniline chain respectively. In the case of fully protonated polyaniline in salt form, the peak at around 590–650 nm disappears and a new peak above 725 nm appears in addition to the appearance of a peak at around 325–360 nm. The peak at 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 the localized polaron band.²⁶

The UV-Vis absorption spectroscopic method was employed to investigate the changes in the optical properties of PANI-H₂SO₄ and PANI-H₂SO₄ containing β -naphthol. The electronic absorption spectra of BN, PANI-BN1-H₂SO₄, and PANI-H₂SO₄ at ambient temperature in dimethyl sulfoxide solvent are shown in Fig. 7. The spectrum of BN showed a peak at 336 nm due to π to π^* transition. The absorption spectrum of PANI-BN1-H₂SO₄ showed two broad peaks at around 400 and 803 nm. However, the absorption spectrum of PANI-H₂SO₄ showed two broad peaks at around 335 and 580 nm with a shoulder peak at around 365 nm. Both the polyaniline salts, PANI-BN-H₂SO₄ and PANI-H₂SO₄, indicate the formation of polyaniline in salt form. However, the absence of a peak above 725 nm in the case of PANI-H₂SO₄ indicates less conjugation, which is the reason for lower conductivity.

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-H₂SO₄ exhibits an emission band at 358 nm. The emission spectrum of PANI-H₂SO₄ containing BN shows peaks at 440 and 460 nm along with shoulder peaks at 415 nm. Thus the appearance of a new emission peak clearly indicates that doping of PANI-H₂SO₄ with BN is perfect and that the BN as well as PANI-H₂SO₄ are not in free form.

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-H₂SO₄ and PANI-H₂SO₄ in the supporting electrolyte of 0.1 M tetrabutylammonium perchlorate in dimethyl sulfoxide (Fig. 9). The energy levels of the HOMO and LUMO were calculated using the following equations:

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

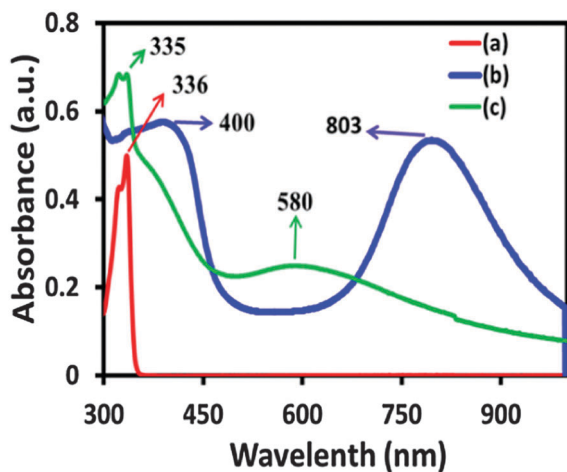
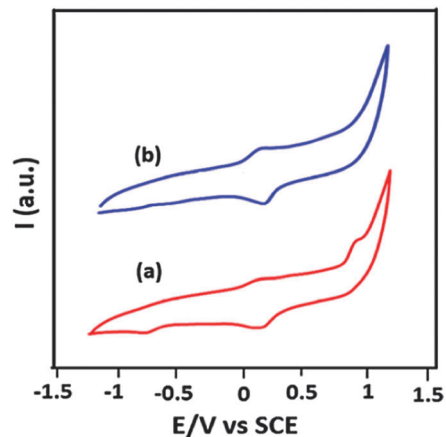
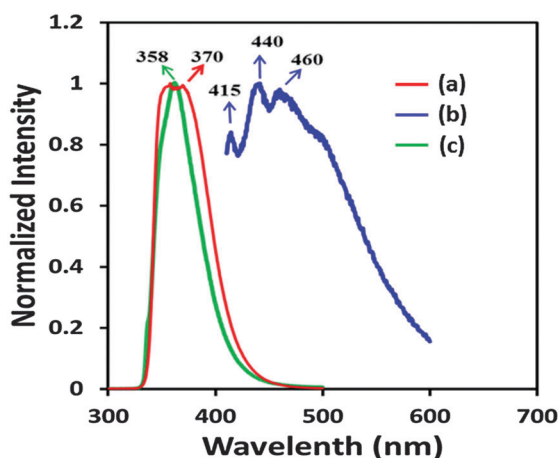
$$E(\text{LUMO}) = -e[E_{\text{red}}^{\text{onset}} + 4.4] \quad (2)$$

The CV of PANI-BN1-H₂SO₄ showed *E* onset oxidation and reduction potentials at 0.91 and −0.55 V respectively. Band gap energy was calculated from the above equation to be 1.46 eV which is very close to that of the energy gap found from the absorption spectrum (1.54 eV). However, only an oxidation

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-H₂SO₄ and (c) PANI-H₂SO₄; i – intense, m – medium, and s – small peak.

Fig. 7 UV-Vis spectra of (a) BN (b) PANI-BN1-H₂SO₄ and (c) PANI-H₂SO₄.Fig. 9 CV of (a) PANI-BN1-H₂SO₄ and (b) PANI-H₂SO₄.Fig. 8 Fluorescence spectra of (a) BN (b) PANI-BN-H₂SO₄ and (c) PANI-H₂SO₄.

potential of 0.92 V was observed for the PANI-H₂SO₄ system (Fig. 9).

Oxidation of aniline by ammonium persulfate with β -naphthol gives polyaniline salt containing dual dopants of β -naphthol and the sulfuric acid group (Scheme 1). Generally, alcohol forms a hydrogen bond with an ammine acceptor.²⁷ In the polyaniline salt, β -naphthol having a hydrogen atom is involved through hydrogen bonding with the nitrogen atom of polyaniline and the 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, sensors, light-emitting diodes, solar cells, and microelectronics.

4. Conclusions

In summary, a 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. The higher conductivity value of polyaniline salts containing dual dopants compared to that of polyaniline-sulfate salt is accounted for higher conjugation and this was concluded from FT-IR, UV-Vis, fluorescence, and CV studies. This novel polyaniline- β -naphthol-sulfuric acid salt was obtained in fiber bundles of 25–80 nm width with thorns at the edge of the fibers. In addition, polyaniline salt showed a highly crystalline nature compared to the conventional polyaniline of semicrystalline nature. Moreover, this polyaniline shows a broad fluorescence spectrum at around 450 nm.

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