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Synthesis, Characterization, and Photoluminescence Properties of 2-amino 6-nitrobenzothiazole-Melamine-Formaldehyde Copolymer-Charcoal Composite

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In this paper, we discuss the photoluminescence (PL) properties of a new copolymer composite synthesized by ultrasonically combining 2-amino 6-nitrobenzothiazole-melamine-formaldehyde copolymer with activated charcoal in a 1:2 molar ratio. Physico-chemical analysis, scanning electron microscopy, and spectral analysis were used to characterize the synthesized copolymer and it's composite. Molecular weight has been evaluated by non-aqueous conductometric titration method. The photoluminescence properties of newblended copolymer-charcoal composite were analyzed using the RF-501 (PC) S CE (LVD) MODEL PL spectrometer. The overall goal of this work is to synthesize new copolymer-charcoal composite and examine their photoluminescent properties, with significant input from current researchers in the field. When the copolymer is excited at 365 nm, it emits intense blue light with a wavelength of 440 nm, which is appropriate for OLEDs.

Keywords: Activated Charcoal, Composite, Copolymer, Photoluminescence, Spectral Analysis

1 Introduction

A composite is a mechanical mixture of two or more constituent materials which neither soluble nor completely merged and have similar physical or chemical properties. Composite materials have drawn interest in both fundamental research and technical applications[1, 2]. This is primarily because changing the size of the incorporated particles allows one to alter the chemical and physical properties of the system. The polymers are appreciably used within the generation of trying to create composite substances inside the matrix that helps to cluster the debris and save you agglomeration, as a matrix in self-assembling substances that promote ordering and anisotropic orientation, as well as acting as a useful detail[3, 4]. The synthesis of polymer-organic composite materials has a number of benefits, including mechanical strength, ease of production, and low cost. They can be made using various techniques such as spin-coating, casting, extrusion, etc., and are distinguished via simple dispensation and control of material shape[5, 6].

In particular, polymer matrices with incorporated semiconducting particles are of interest to the field of organic electronics. The improvement of expedients that combine the variety and processability of organic materials with tremendous electrical and optical performance of inorganic crystals is achieved by the integration of organic and inorganic constituents into hybrid optoelectronic structures. The incorporation can increase the effectiveness of organic light emitting diodes (OLEDs) and give one the option to choose the shades of the emission simple mixing an effective emission from each of the two materials [7, 8]. Recent studies emphasized on the luminescence characteristics of semiconducting polymers and some of their composites with inorganic nanoparticles. Due to the quantum size effect, changing the nanocrystal size can change the emission's colour[9]. Recent research has demonstrated that the same composite layer can emit many colors of electroluminescent (EL) and photoluminescent (PL) light when the emitting color is altered by an applied electric field[10, 11]. Electric field-controlled green-to-red colour swapping of EL/PL emission has been seen in the MEH-PPV:ZnO composite[12].

In photoluminescence spectroscopy (PL), light energy or photons are transmitted through the sample, absorbed, and excess light energy is released into the sample. This approach of material exploration is

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nondestructive and noncontact. It is a potent method for characterizing and analyzing the electrical structure of intrinsic and extrinsic semiconducting and semi-insulating materials. Numerous copolymer composites have been developed and employed successfully during the past three decades as electron-transporting and emitting components in OLEDs, selective luminescence sensors, as well as non - linear optical substances. Karimi and co-workers studied the photoluminescent properties of PS/PPO/CeF3 nanocomposites and observed that synthesized nanocomposite was useful for the fabrication of organic scintillators for radiation detection devices[13].

Tetraphenylethylene and spiropyran were used as the monomers in the formation of the amorphous polyacrylamide copolymer TPE-SP-PAM by Gu and coworkers[14]. This material combines photochromism and white-light emission, leading to a new development in the formation of stimuli-responsive polymeric materials with multicolor emissions. Thermoresponsive, Amphiphilic, rod-coil conjugated P3HT-bPNIPAM block copolymer was synthesized by Bera et. al. from poly(3-hexyl thiophene) and poly (N-isopropylacrylamide). This block copolymer is thought to be a potential material for sensor, fluorescence thermometer, optoelectronic, as well as bioelectronic devices due to its distinct electronic and optical properties[15]. To synthesize blue-light emission, NPPV block copolymer was accomplished by utilizing the Horner-Emmons condensation polymerization method[16]. 8-hydroxyquinoline-1,6-diaminohexane-formaldehyde and co-polymeric metal complexes with Cu^{+}, Ni^{+2}, and Zn^{+2} were examined for their photoluminescence spectra by W. B. Gurnule and colleagues[17]. S. Basu *et al.* investigated the photoluminescent characteristics of poly(styrene-b-2-(N,N-dimethylamino)ethyl methacrylate) diblock copolymers[18].

The goal of this study is to produce copolymer derived from the 2-amino 6-nitrobenzothiazole, and melamine with formaldehyde and its composites with activated charcoal. The formed copolymer was evaluated using FTIR, ^{1}H NMR, UV-Visible, and FTIR Spectral techniques. SEM was used to analyze the morphology of copolymers and the composites produced from them. In this paper, we explain the methods and methodologies we utilized to analyze our synthesized copolymer composite and explore the physical science that underlies the behavior of light-emitting polymers.

2 Materials and Methods

2.1 Materials

The synthesis was carried out using only the purest, analytical-grade chemicals and solvents. 2-amino-6-nitrobenzothiozole (Sigma Aldrich), Melamine (Merk India), Formaldehyde (Merk 37%), Dimethyl suphoxide (99.8%, Fisher Scientific), and Dimethylformamide (99% Genni Chem).

2.2 Synthesis of BMF-IV copolymer

By condensing 2-amino 6-nitrobenzothiazole (6.6 g, 0.4 mol), melamine (2.5 g, 0.2 mol), and formaldehyde (26.25 mL, 0.7 mole) in the presence of 2 M HCl (200 mL) as a catalyst at 122°C in an oil bath for 5 hours, the BMF-IV copolymer was synthesized. Once the reaction period was over, the yellow solid product acquiredwas detached from the round bottom flask. The obtained product was washed with cold water, dried, and pulverized. To get eliminate unreacted monomers, the powder was repetitively rinsed using cold water. By dissolving it in 8% NaOH and filtering the resulting solution, it was further purified. In Fig. 1, a schematic representation of the BMF-IV copolymer synthesis is shown.

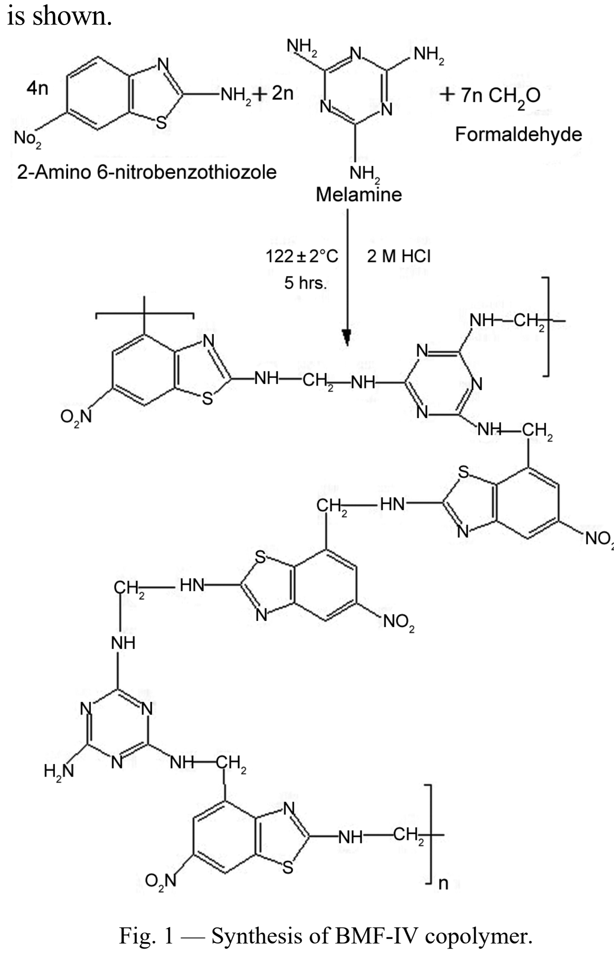

Fig. 1 — Synthesis of BMF-IV copolymer.

Table 1 — The Physicochemical and Analytical Data of the BMF-IV Copolymer

Copolymer	The empirical formula of repeating unit	Empirical formula weight	%C Found (Cal.)	% H Found (Cal.)	% N Found (Cal.)	% S Found (Cal.)
BMF-IV	$C_{41}H_{32}N_{23}O_8S_4$	1102	44.09 (44.64)	2.43 (2.90)	28.94 (29.22)	11.47 (11.62)

2.3 Preparation of Copolymer composites with activated charcoal

Activated charcoal (2.0 g) and copolymer (1.0 g) were combined in a 1:2 ratio to produce the novel copolymer/activated charcoal composite. Activated charcoal was added to the copolymer, which had been solubilized in 25 ml of DMSO, in a 100 ml beaker. The mixture was then ultrasonically processed for 3 h at room temperature with constant stirring. After a certain time, the black color composite was obtained, separated, washed off impurities using ethanol and acetone, filtered, and dried for 24 h at 70°C.

2.4 Instrumentation

The copolymer was micro-analyzed using an Elementer Vario EL III elemental analyzer (Germany) for C, H, and N elements. Infrared spectra of the copolymer and its composite with activated charcoal were recorded in the range of 4000 to 400 cm^{-1} using a Bruker Alpha-E FTIR spectrophotometer at the Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur. A UV-1800 Shimadzu automatic recording double beam spectrophotometer was used by Shivaji Science College in Nagpur to record the electron absorption spectra of the copolymer and their composite in the 200 to 800 nm range of the DMSO solvent. The copolymer and its composites were scanned and magnified using a scanning electron microscope at the STIC, Cochin, and SAIF, Dharwad University respectively. At Kamla Nehru Mahavidyalaya in Nagpur, the photoluminescence spectra of the BMF-IV copolymer have been measured using a Shimadzu MODEL RF-5301(PC) S CE (LVD) LS55 spectrophotometer.

3 Results and Discussion

3.1 Physical-chemical and elemental analysis

The formed BMF-IV copolymer was yellow. The newly synthesized copolymer was discovered to be unsolvable in nearly all organic solvents, but soluble in solvents like THF, DMF, DMSO as well as conc. H_2SO_4. The yield of the copolymer was found to be 8 %. When dissolved in DMSO, the BMF-charcoal composites were discovered to be soluble. The hydrogen, carbon, sulphur, and nitrogen percent

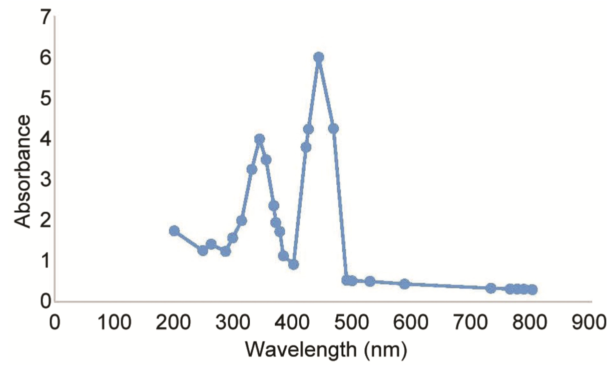

Fig. 2 — UV-Visible spectra of (a) BMF-IV copolymer, & (b) Composite.

compositions of the copolymer were investigated. The copolymer's empirical formula and empirical formula weight has been determined as a result of elemental analysis, and they are displayed in Table 1.

3.2 UV-Visible Spectral Analysis

According to Fig. 2, the 200-800 nm range of the UV-visible spectra of the BMF-IV copolymer and its composites have been characterized in DMSO solvent. The newly made BMF-IV copolymer, which is shown in Fig. 2(a), has two distinct bands at 269 nm and 360 nm. The band observed at 269 nm has less intensity because of the allowed $\pi\rightarrow\pi^*$ transition. Because of the benzothiazole ring, the allowed $\pi\rightarrow\pi^*$ transition is obtained. The $n\rightarrow\pi^*$ transition, which indicates the presence of -NH auxochrome, may also be the cause of the intense band at 360 nm. The $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ transitions, respectively, demonstrate the existence of aromatic nuclei and -NH groups. Hyperchromic shift (εmax higher values) is caused by the presence of -NH groups (auxochromes)[19, 20].

As shown in Fig. 2 (b), the UV-Vis spectra of the composite exhibit two absorption bands at 250 nm and 330 nm. The absorption band at 250 nm, which may be caused by the $\pi\rightarrow\pi^*$ transition, clearly indicates the existence of an aromatic ring (i.e. the benzothiazole ring) in the composite. The -NH group can be observed in the composite at 330 nm, which is attributed to the $n\rightarrow\pi^*$ transition. The shifting of bands, as shown in Fig. 2, is evidence that composites have been formed. The results also showed that, in comparison to copolymers, the absorption of

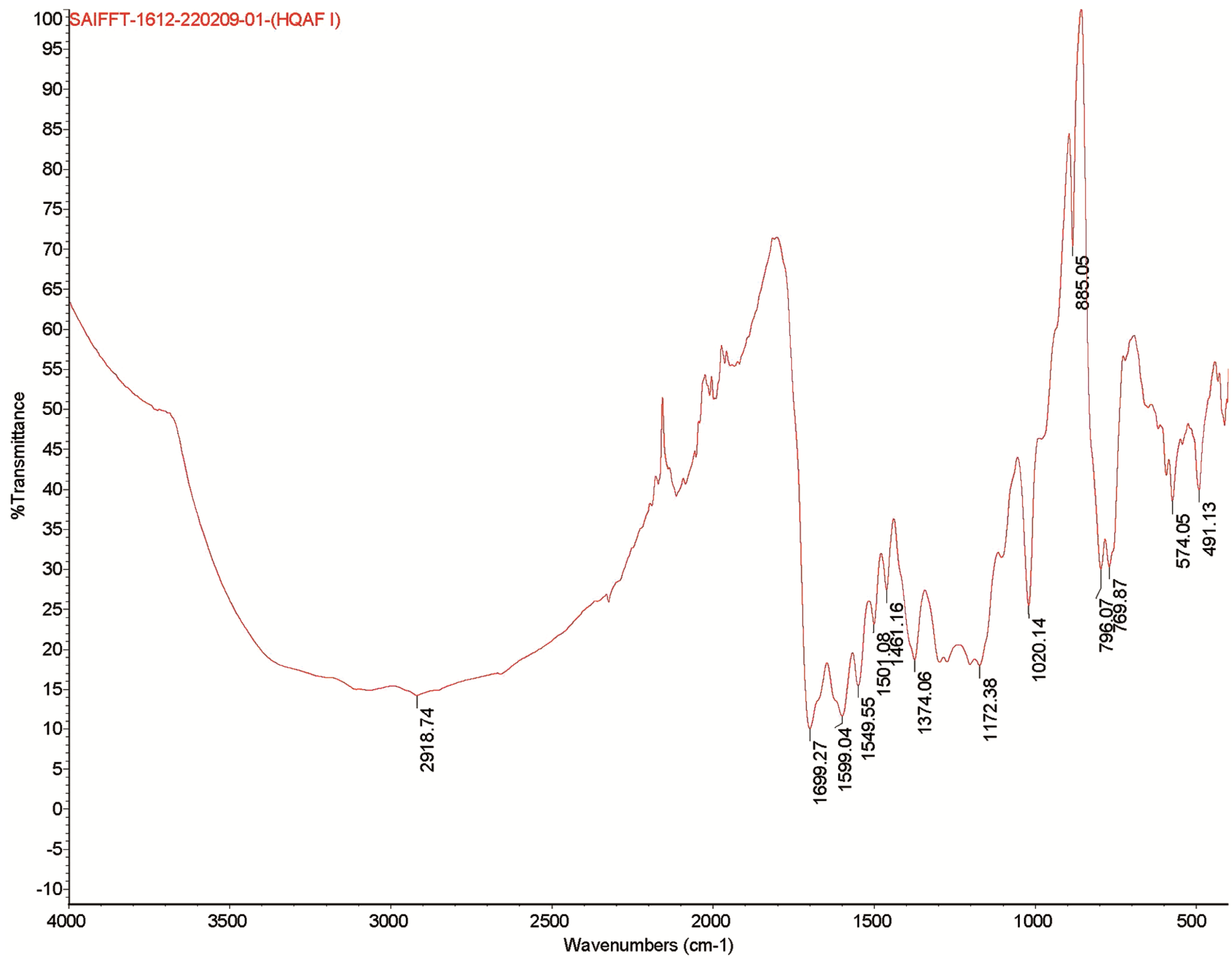

Fig. 3 — FTIR spectra of (a) BMF-IV copolymer, & (b) Composite.

composites decreased. The formation of composites was established as a result of the aforementioned factors[21, 22].

3.3 FTIR spectra

The chemical structure of the newly formed copolymer its composite, which includes several functional groups, was validated using the FTIR spectra in Fig. 3. The copolymers as well as their composite exhibit a nearly identical spectra pattern, according to IR spectra. Figure. 3(a) displays the FTIR spectra of the newly synthesized BMF-IV copolymer. The copolymer's band frequencies and designated groups have been identified by previous research [23,24]. The band formed at 3618 cm^{-1}due to the -NH asymmetric as well as symmetric vibrations. The $-NO_2$ group of the benzothiazole ring stretching mode is due to the appearance of band at 1520 cm^{-1}. Sharp and medium absorption bands in the 1175-774 cm^{-1} range are produced by the 2, 6, 8-trisubstituted benzothiazole ring of the copolymer. The absorption band formed by 3012 cm^{-1} indicated the presence of -CH_2 asymmetrical and symmetrical vibrations in the BMF-IV copolymers. A band at 2942 cm^{-1} has been designated for the aromatic ring`s -CH stretching vibrations. The band appeared at 1440 cm^{-1} shows that the N-CH_2-N Bridge in the copolymer has a -CH_2 bending vibration. The presence of the C-S-C group is confirmed by the band at 750 cm^{-1}, whereas the C=N stretching mode of the thiazole ring is responsible for the band at 1679 cm^{-1}.

Figure. 3(b) displays the FTIR spectra of the composite. The results show that the spectrum of composites and the spectrum of copolymers are only slightly different[25]. The asymmetric and symmetric vibrations of the -NH group produced by copolymers are represented by the band at 3737 cm^{-1}. This effectively demonstrates how composites are formed. Additionally, the benzothiazole ring's $-NO_2$ group stretching mode results in a band at 1584 cm^{-1}. The aromatic ring's -CH

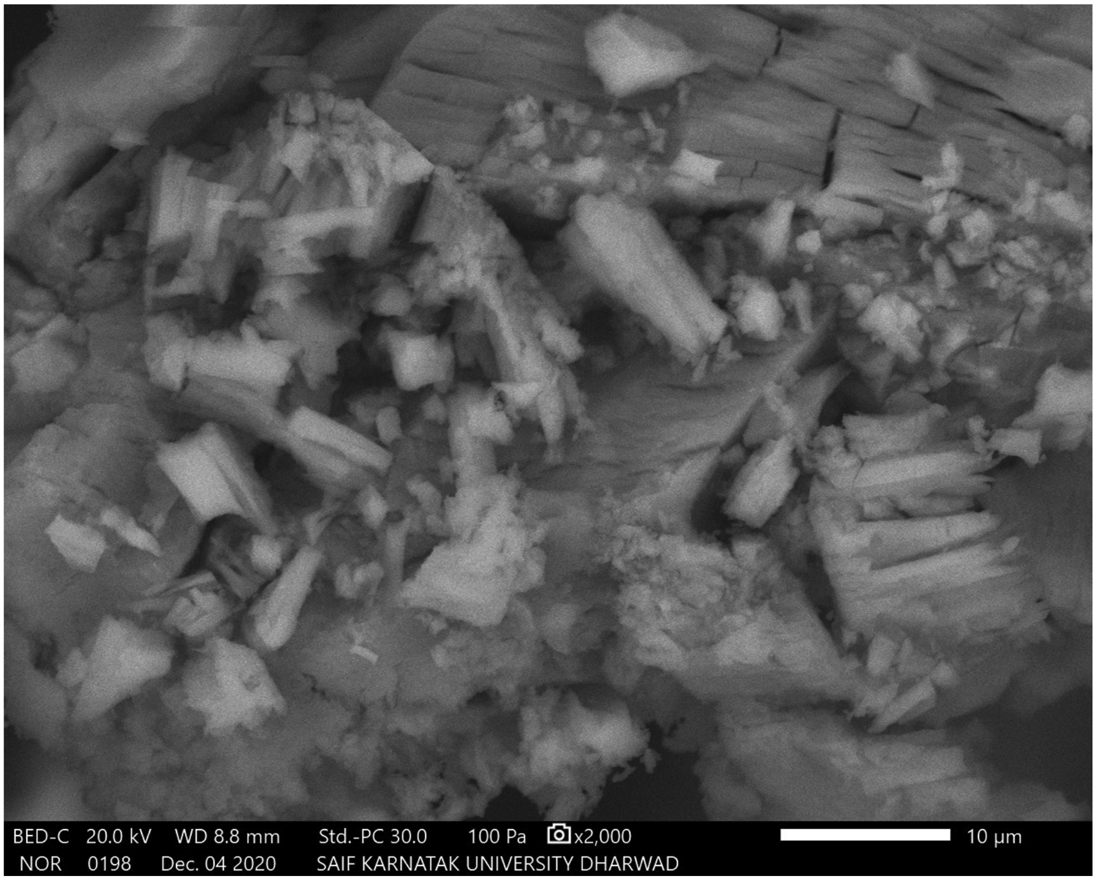

Fig. 4 — SEM images of (a) BMF-IV copolymer, & (b) Composite.

stretching vibrations produce the band at 2991 cm-1. The -CH2 asymmetric and symmetric vibrations in copolymer is confirmed by the formation of band that formed at 3120 cm-1. The presence of a 1478 cm-1 absorption band confirms the existence of a-CH2 bending vibration in the N-CH_2-N bridge. From 1305 to 797 cm-1, the 2, 6, 8-tri substituted benzothiazole ring produces distinct, medium/weak absorption bands. The band at 939 cm-1 confirms the existence of the C-S-C group. The formation band at 1655 cm^{-1} is due to the thiazole ring's -C=N stretching. The different bands observed designate that the copolymers and charcoal interact. The copolymers and activated charcoal composites were successfully created under the specified conditions.

3.4 Scanning electron microscopy

The surface characteristics of the BMF-IV copolymer and their composite with activated charcoal were examined using scanning electron micrographs at various magnifications, displayed in Fig. 4. It details the surface topography and defects of the structure. Similar to the irregular granular particles depicted in Fig. 4, the BMF-IV copolymer has a confined packed structure with deep pits as well as numerous active sites. The newly formed copolymer is porous, and SEM images of the BMF-IV copolymer showed a fringed representation of the semi crystalline structure. The micrographs' fringes show that the copolymer is transitioning from an amorphous state to a crystalline one. The crystalline structure of the monomer is changed by polymerization into the amorphous phase of the copolymer. Air voids may cause few noticeable cracks and holes[26, 27]. The composite's SEM images are displayed in Fig. 4. Comparing the composite to a copolymer, the surface morphology shows an excess of active particles. The external morphology of the composite shows an extra of active spots and diverseholes as likened to copolymer. This suggests that increasing the composite's surface area caused more cavities to form. The pictures show that the synthesized copolymer and activated charcoal, which has more active sites and a larger surface area, formed very firmly in the composite[28-33].

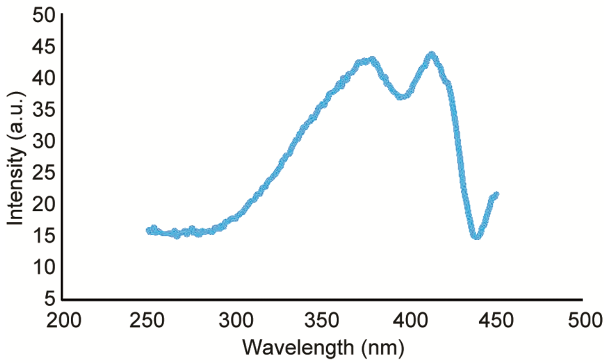

Fig. 5 — PL (Excitation) Spectra of BMFC-IV Composite.

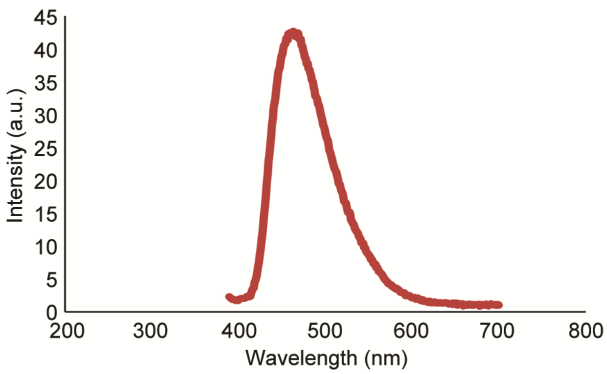

Fig. 6 — PL (Emission) Spectra of BMFC-IV Composite.

3.5 Photoluminescence study of BMF copolymer-charcoal composite

At Kamla Nehru College in Nagpur, the photoluminescence spectra of the BMF copolymer-charcoal composite were measured using a Shimadzu MODEL RF-5301(PC) S CE (LVD) LS55 spectrophotometer. Localized π-electron systems within certain molecules govern the luminescence of organic compounds to a large extent. Figure. 5 shows the BMFC-IV composite's emission spectrum. The emission has a maximum wavelength of 470 nm and is in the blue region, in addition to having excitation spectra at 389 nm and 411 nm. As seen in Fig. 6, when composite is excited, it emits strong blue light with a wavelength of 470 nm, which is suitable for OLEDs.

Charge transfer from the copolymer to the activated charcoal, or carbon, responsible for the luminescence phenomenon in composite. This may be the result of adding charcoal, or carbon, to the conjugated copolymer. Carbon interacts with the highly delocalized π -electrons correlated with the copolymer backbone chain to increase the quantum efficiency of conjugated copolymers. This shows that there is good charcoal percolation in the copolymer matrix, which accelerates photo-induced charge transfer. As a result of the implied charge transfer, it is possible for charcoal to act as an electron trap for photoinduced excitons[34].

4 Conclusion

By polycondensing 2-amino 6-nitobenzothiazole and melamine with formaldehyde in a 4:2:7 molar ratio, the BMF-IV copolymer was synthesized with good yield. Its composite was then formed by ultrasonically combining activated charcoal in a 1:2 ratio. When the FTIR and UV-Visible spectra of a copolymer and its composite are compared, the shifting of bands verifies the creation of composites. The surface morphology suggests that the BMF-IV copolymer exhibits a phase transition between the crystalline and amorphous states. Additionally, SEM micrograph demonstrates that the composite has more active sites and distinct pores than copolymer, which is due to the composite's higher surface area. The copolymer composites exhibited photoluminescence properties due to the modification of copolymer matrix by the addition of charcoal as a filler. Consequently, the conducting copolymer-charcoal composites are the preferred materials for the fabrication of low-cost photovoltaic devices.

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