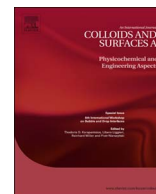




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## Colloids and Surfaces A

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# Change of optoelectronic parameters of the boric acid-doped polyaniline conducting polymer with concentration

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## ABSTRACT

In this study, boric acid (BA)-doped polyaniline (PAni) conducting polymer (PAni-BA) was chemically synthesized in the emeraldine salt form using  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as an oxidant agent. The structural and morphological properties of PAni-BA were characterized by Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric analysis (TGA) and Scanning Electron Microscopy (SEM) analyzes. The sensing and optical properties of the PAni-BA solutions prepared in dimethylsulfoxide (DMSO) were firstly examined. The effects of concentration on optoelectronic parameters and single oscillator model parameters of the PAni-BA solutions were investigated. Finally, electrical and optical conductance values of the PAni-BA were compared. It was observed that the PAni-BA can be used for the fabrication of many optoelectronic devices due to its suitable optical properties and low optical band gap.

## 1. Introduction

Conducting polymers are known as organic semiconductors due to their vulnerable electronic properties. They have been used various application areas such as electrochemical devices, photodiodes, batteries, sensors, and solar cells [1–3]. Among the conducting polymers, PAni has great importance. Generally, PAni is chemically synthesized by using radicalic-oxidative polymerization method which is using an oxidant agent to generate the radicals. The polymerization of PAni occurs in pH < 7 media and the acidic media cause the head-to-tail coupling of the radicals in the para position [4]. PAni exists in a variety of protonation and oxidation forms. Its green protonated emeraldine salt form is electrically conducting, because of the cationic radicals in its structure. It can be dedoped by using NaOH solution to produce emeraldine base form. Ease of synthesis, chemical stability, controllable conductivity and solubility are among its important features [5–9].

Recently, many studies have reported on doping of PAni. In a study, the effects of several organic acids (acetic, citric, oxalic, and tartaric acid) as dopant ions on PAni properties were investigated. Among these doping agents, oxalic acid was determined to be more suitable as a protonic acid media for PAni with high conductivity [10]. The  $\text{Cu}^{+2}$  ion doped PAni particles were also synthesized by oxidative polymerization of aniline. Conductivity of the  $\text{Cu}^{+2}$  ion doped PAni was found to be change with the amount of the  $\text{Cu}^{+2}$  ions and there was an optimum concentration of  $\text{Cu}^{+2}$  ions for the highest conductivity [11]. In another

study, bismuth nitrate doped PAni was reported and it was found that PAni doped with  $\text{Bi}(\text{NO}_3)_3$  showed a higher value of conductivity which was 2.5-fold higher than HCl doped PAni [12].

On the other hand, boric acid (BA) particles have been used in various studies for boron doping, since BA has some advantages such as industrial importance and low-cost. In a study, poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) doped with BA layers were synthesized and their effects on the solar cells based organic molecules were investigated [13]. The films of PEDOT:PSS doped with BA were prepared by using spin coating method and their structures were confirmed by FTIR, UV, XRD, AFM, and conductivity measurements. Their results demonstrated that the fill factor (FF) and open-circuit voltage ( $V_{oc}$ ) values increased with interaction of the PEDOT:PSS layers with BA dopant. The monolayer graphene doped by using BA (boron) and urea (nitrogen) was reported [14]. It was found that the synthesis of boron and nitrogen doped graphene is considered to be an effective method to obtain graphene sheets with high electrical and optical performances and low cost. The dye sensitized solar cells based on titanium dioxide ( $\text{TiO}_2$ ) nanotubes doped with BA was studied [15]. The BA doped  $\text{TiO}_2$  nanotubes exhibited higher performance than undoped  $\text{TiO}_2$  nanotubes and the conduction band shifted due to introduction of boron into the interstitial sites of  $\text{TiO}_2$  lattice. These suggest that BA is a potential doping agent to improve electrical and optical properties of the materials.

Optoelectronics plays an important role on applications such as

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solar cells, flat screen TVs, laser, computer displays, light-emitting diodes (LEDs), high-speed communication devices, optical sensors, etc. of polymer and semiconductor optoelectronic devices. Optoelectronic parameters give useful and significant data about optoelectronic devices. Several studies on optoelectronic properties of PANi derivatives such as PANi doped with dodecyl benzene sulfonic acid (DBSA) [16], RNA–PANi–dendritic gold [17], PANi:TiO<sub>2</sub> [18] and PANi–CdS nanocomposite [19] have been reported by using different techniques. Solution technique for determination of the optical properties of the soluble polymers has high accurate results and low cost when it is compared with other techniques. To the best of our knowledge, the effects of concentration on optoelectronic parameters of the PANi–BA solutions have not hitherto been reported in the literature.

Therefore, the aims of the present study are to investigate the effects of concentration on optoelectronic properties of PANi–BA conducting polymer dissolved in DMSO, to determine the many significant optoelectronic parameters for different concentrations, and to examine the usability of PANi–BA conducting polymer for optoelectronic devices.

## 2. Experimental

### 2.1. Materials

Aniline monomer (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>) was purchased from E. Merck (Germany) and used after vacuum distillation. (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (APS) and DMSO were also obtained from E. Merck (Germany) and used as initiator and solvent, respectively. Boric acid (BA), B(OH)<sub>3</sub>, was purchased from Aldrich (Germany) and used as doping agent. All the other chemicals used in the experimental studies were purchased from E. Merck (Germany) with analytical grade and used as received without further purification.

### 2.2. Synthesis of PANi–BA conducting polymer

Conducting PANi–BA was synthesized by radical-oxidative polymerization method. For this purpose, 5.0 g aniline was added in pre-cooled (0–5 °C) 150 mL 1 M B(OH)<sub>3</sub> solution and stirred for 30 min under reflux. On the other hand, pre-cooled (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution (0–5 °C) was prepared in 50 mL 1 M B(OH)<sub>3</sub> solution. The molar ratio of (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> to aniline was taken as 2:1. The (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution was added dropwise into the aniline/B(OH)<sub>3</sub> solution at the same temperature. The polymerization was carried out under N<sub>2</sub> atmosphere for 16 h. The crude product was filtered and then washed several times with distilled water to remove any impurities present, and dried at 60 °C for 24 h. The dark green product was recovered with 95% yield and coded as PANi–BA. Then, optoelectronic parameters of the PANi–BA conducting polymer were examined.

### 2.3. Characterization

The PANi–BA particles were milled to reduce particle size distribution by using a Retsch MM400 model milling machine (Germany) and then following characterizations were carried out. Structural analysis of the sample was performed by Perkin Elmer BX FTIR model Spectrometer (England). Thermo-gravimetric analysis of the sample was performed by using a Perkin Elmer Diamond model TGA/DSC instrument (U.S.A.). The TGA data was collected in the range of 25–900 °C under N<sub>2</sub> atmosphere. Surface image of the sample was monitored with a JEOL JSM 5500LV model SEM instrument (Japan).

### 2.4. Preparation of the PANi–BA conducting polymer solutions

The PANi–BA sample was weighed to prepare the solutions with a AND-GR-200 Series Analytical Balance. The solutions of PANi–BA in DMSO were prepared at 0.8, 2.4 and 4.8 g/L concentrations using digital vortex mixer (Four E's Scientific CO., Ltd.). The real image of the

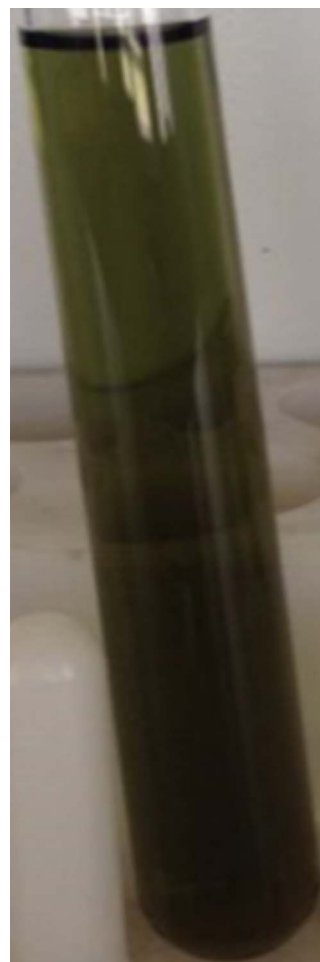


Fig. 1. The real image of the PANi–BA solution in DMSO for 0.8 g/L concentration.

PANi–BA solution for 0.8 g/L is shown in Fig. 1.

### 2.5. The UV measurements of the solutions

A cylindrical bathtub (Hellma QS-100) was used for the PANi–BA solutions. The UV measurements of the solutions for 0.8, 2.4 and 4.8 g/L were performed by using UV-1800 Spectrophotometer (Shimadzu model) at room temperature.

## 3. Results and discussion

### 3.1. Characterization results

Fig. 2 depicts the FTIR spectrum of PANi–BA conducting polymer.

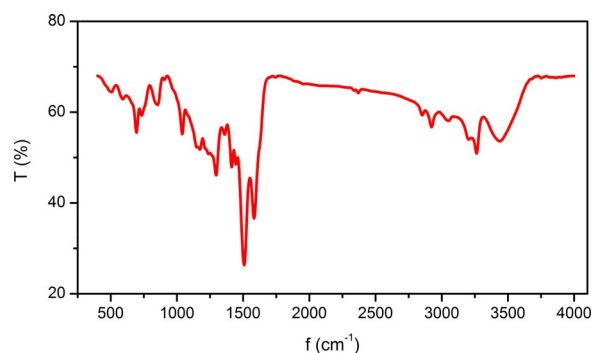


Fig. 2. FTIR spectra of the PANi–BA conducting polymer.

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