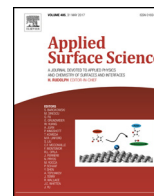




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Full Length Article

Controlling the optical properties of polyaniline doped by boric acid particles by changing their doping agent and initiator concentration

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ABSTRACT

In this study, polyaniline doped by boric acid (PAni:BA) conducting polymers were chemically synthesized by oxidative polymerization method using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (APS) as initiator. PAni:BA conducting polymers were synthesized by using two different APS/aniline molar ratios as 1:1 and 2:1. Their results were compared with PAni doped by HCl (PAni) conducting polymer. Structural properties of the PAni, PAni:BA (1:1) and PAni:BA (2:1) conducting polymers were characterized by using FTIR, SEM, TGA, particle size and apparent density measurements. Effects of doping agents and initiator concentrations on optical properties were investigated in detail. The optoelectronic parameters such as absorption band edge, molar extinction coefficient, direct allowed band gap, refractive index, optical conductance and electrical conductance of the PAni, PAni:BA (1:1) and PAni:BA (2:1) were determined. The absorption band edge and direct allowed band gap of PAni were decreased with doping BA and increasing APS ratio. Also, the refractive index values of the materials were calculated from experimental results and compared with obtained results from Moss, Ravindra, Herve-Vandamme, Reddy and Kumar-Singh relations.

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1. Introduction

Increasing usage of conducting polymers has accelerated studies on polymer applications in recent years. Conducting polymers with long π -conjugated structures have unique properties such as flexibility, thermal and electrical stability, ease of synthesis and durability [1]. The conductivity of the conjugated polymers is achieved through chemical oxidation or reduction reactions by using a series of simple anionic or cationic species called dopant [2]. Also, in order to modify the transport, optical and mechanical properties of the conducting polymers, dopant agents can be added directly to this polymers [3,4].

Polyaniline (PAni) is one of the most popular one among the conducting polymers due to environmental stability, ease of synthesis, adjustable conductivity, amazing chemical, electrical and optical properties [5]. PAni and its derivatives are used in various industrial areas such as electrochromic devices, sensors, toners, conductive paints, drug delivery, rechargeable batteries electrolytes, transistors, solar cells and electrorheological applications [5–8].

Among the doping agents, boric acid (BA) particles have been used in various studies for boron doping process. Sevinis et al. have reported the optoelectronic properties of soluble copolymers composed of dithienothiophenes (DTT), DTT-4,4-dioxide (DTT-S,S-O₂) donor and esitylboryl acceptor units. Their results showed that the band gap values increased to 2.46–3.21 and 2.18–2.88 eV due to an intramolecular charge transfer transition between the donor DTT units and the boron acceptor atoms, respectively [9]. Yagci et al. Synthesized the poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) doped with BA layers and investigated their effects on the solar cells based organic molecules. Their results showed that the fill factor (FF) and open-circuit voltage (V_{oc}) values increased with interaction of the PEDOT:PSS layers with BA dopant [10]. Subramanian and Wang have reported the dye sensitized solar cells based on TiO₂ nanotubes doped with BA. The conduction band of doped nanotubes shifted to lower values due to introduction of boron into the interstitial sites of TiO₂ lattice [11]. Wu et al. synthesized the monolayer graphene doped by boron and urea (nitrogen). Their results showed that the doping of graphene by nitrogen and boron caused to increase in the electrical and optical performance of the graphene sheets [12]. According to these studies, it was concluded that BA is an effective doping agent to improve electrical and optical properties of the materials.

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Optical parameters have a significant role on various properties of organic electronic, photonic and optoelectronic applications such as displays, lasers, light emitting diodes, diodes, solar cells, photovoltaics, transistors, photodetectors, electroluminescent sensors, optical waveguides, radio frequency identification tags and smart cards [13]. The molar extinction coefficient is parameter to define the absorbance intensity at a given wavelength per molar concentration [14,15]. The optical band gap and refractive index are fundamental parameters for optoelectronic materials [16,17]. The optical band gap gives many useful clues about various properties of the materials. The imaginary part of the refraction index gives the intensity attenuation inside the medium, while the real part of the refraction index is inversely proportional to the wave propagation velocity [18].

Effects of the APS initiator concentration on optical properties of the soluble PANi:BA conducting polymers have not hitherto been reported in the literature. Therefore, the aim of the present study was to investigate the optical parameters of PANi:BA conducting polymers synthesized in two different initiator ratios ($n_{\text{APS}}/n_{\text{aniline}} = 1:1$ and $2:1$). Since PANi is generally doped in HCl medium, the results obtained were compared with that of PANi doped by 1 M HCl(aq) ($n_{\text{APS}}/n_{\text{aniline}} = 1:1$).

2. Experimental

2.1. Materials

Aniline monomer ($\text{C}_6\text{H}_5\text{NH}_2$) was used after vacuum distillation (E. Merck, Germany). Boric acid, $\text{B}(\text{OH})_3$, was purchased from Aldrich (Germany) and used as doping agent. All the other chemicals used in the experiments (HCl, APS, dimethylsulfoxide (DMSO) etc.) were purchased from E. Merck (Germany) with analytical grade and used as received without further purification.

2.2. Synthesis of PANi and PANi:BA conducting polymers

0.05 mol aniline was dissolved in 1 M $\text{B}(\text{OH})_3$ and stirred for 30 min at $0-5^\circ\text{C}$ temperature. Then, pre-cooled ($0-5^\circ\text{C}$) APS solution by taking $n_{\text{APS}}/n_{\text{aniline}} = 1:1$ was prepared in 1 M $\text{B}(\text{OH})_3$. This solution was added dropwise to the aqueous solution containing aniline and $\text{B}(\text{OH})_3$ at $0-5^\circ\text{C}$ temperature. The mixture was kept stirring under N_2 atmosphere at $0-5^\circ\text{C}$ for 16 h under reflux. Then, the crude product in dark green color was filtered, washed with distilled water and dried at 60°C under vacuum. Also, PANi doped by BA by taking $n_{\text{APS}}/n_{\text{aniline}} = 2:1$ was synthesized with the same method. The synthesized PANi:BA (1:1) and PANi:BA (2:1) conducting polymers were obtained with 93% and 95% yield, respectively. To compare the effects of BA with HCl doping agent, PANi was synthesized with the same method in 1 M HCl(aq) at $0-5^\circ\text{C}$ by using APS ($n_{\text{APS}}/n_{\text{aniline}} = 1:1$). PANi doped by HCl was obtained with 87% yield and coded as PANi. Thus, PANi and PANi:BA (1:1) and PANi:BA (2:1) conducting polymers were used for the determination of optical parameters.

2.3. Characterizations

To obtain small and homogeneous particle size distributions, the materials were ground milled by using a Retsch MM400 model milling machine (Germany) and subjected to the following characterizations. FTIR spectra of the materials were conducted as KBr discs using a Perkin Elmer Spectrometer BX FTIR system (England). Thermal analyses of the materials were performed with a Perkin Elmer Diamond thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) thermal analysis instrument (U.S.A.). The specimens were heated at a rate of $10^\circ\text{C}/\text{min}$ under N_2 atmosphere from room temperature to 900°C . The surface morphology

of the samples were examined by using a JEOL JSM 5500LV (Japan) scanning electron microscope (SEM). Hydrodynamic particle size of the samples was determined by dynamic light scattering (DLS) using Malvern Zeta-Sizer Nano ZS (England). The self-optimization routine (laser attenuation and data collection time) in the Zeta-Sizer software was used for all the measurements. The samples were turned into pellets using a steel die of 13 mm diameter and their apparent densities were calculated from masses and volumes of the pellets.

2.4. Preparation of the solutions

The solubility of the materials is very important for preparation of the optoelectronic devices. A defined amount of PANi, PANi:BA (1:1) and PANi:BA (2:1) conducting polymers were taken to prepare their solutions with a AND-GR-200 Series Analytical Balance and dissolved homogeneously in 12 mL volume of DMSO solvent using digital vortex mixer (Four E's Scientific CO., Ltd.).

2.5. The UV measurements of the solutions

A cylindrical bathtub (Hellma QS-100) whose optical path length is 10 mm and volume is 3.5 mL was used for all the solutions of the PANi, PANi:BA (1:1) and PANi:BA (2:1) conducting polymers. The UV measurements of the materials were recorded with a Shimadzu model UV-1800 Spectrophotometer at room temperature.

3. Results and discussion

3.1. Characterization results

FTIR spectra of the PANi, PANi:BA (1:1) and PANi:BA (2:1) were depicted in Fig. 1. As shown that PANi had characteristic stretching bands of $-\text{NH}$ (3250 cm^{-1}), aliphatic $-\text{CH}$ (2950 cm^{-1}), $\text{C}-\text{C}$ and $\text{C}-\text{N}$ (1700 cm^{-1}), and aromatic benzene (820 cm^{-1}). PANi:BA (1:1) and PANi:BA (2:1) conducting polymers showed similar spectra and the peaks at $3200-3450\text{ cm}^{-1}$ due to $\text{N}-\text{H}$ stretching; at 2920 cm^{-1} due to aliphatic $\text{C}-\text{H}$ stretching; at $1580-1450\text{ cm}^{-1}$ due to $\text{C}-\text{C}$ and $\text{C}-\text{N}$ stretching of quinoid and benzenoid rings of PANi; $1100-1300\text{ cm}^{-1}$ due to aromatic stretching; $750-800\text{ cm}^{-1}$ due to $\text{C}-\text{H}$ bending of 1,4-disubstituted benzene ring. When the absorption bands of PANi:BA (2:1) were compared with that of PANi:BA (1:1), some shifts were observed in the peak values and intensities. These shifts can be attributed to increasing polymerization ratio of aniline with increasing initiator molecules in the solution and hydrogen-bonded interactions between conducting PANi chains. Similar effects were observed in literature for polyaniline-graft-chitosan copolymer [19] and self-assembled nano/microstructured polyaniline-clay nanocomposite [20]. The

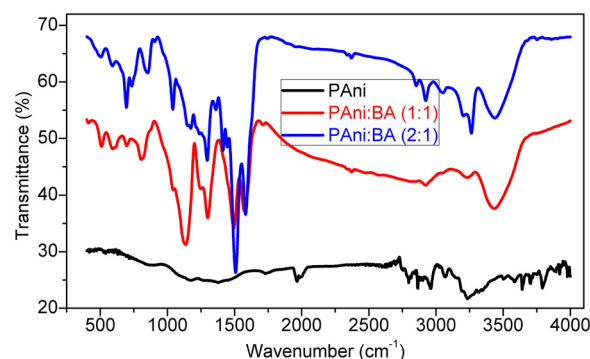


Fig. 1. FTIR spectra of the conducting polymers.

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