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Electrochemical Synthesis and Characterization of ZnO Nanocomposite Copolymer Containing Fluorescent Feature Dye

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Abstract. BODIPY (boron dipyrrolmethene) has attracted the attention of scientists although the synthesis of BODIPY from the fluorescent dye class is challenging, there are many applications such as fluorescence, ion / molecule and pH probes, sensors, redox active molecules, metal chelators, cellular imaging, photodynamic therapy, drug delivery materials and photovoltaic applications and energy storage. Firstly, it is synthesized with difficulty in synthesis but attractive fluorescence active monomer. Then, by electrochemical method, a conductive copolymer, which is an innovative material, was synthesized. The nanocomposite was synthesized with the help of a potentiostat using Zno nanoparticles to increase the strength and conductivity properties of the obtained semiconducting material and its existence was determined by advanced technological devices such as SEM-EDX, AFM-Raman. Characteristic peaks of inorganic and nano-scale compounds such as ZnO are observed in the fingerprint region and weak / medium in the conventional FT-IR device. This makes it difficult to qualitatively diagnose the compounds by infrared spectrometry. Raman spectroscopy, however, has been preferred for the determination of nanoparticles because it is relatively laborious, such as ICP-MS, and is not a complex spectral region such as FT-IR.

Keywords**:** Conducting Polymer, Nanocomposite, AFM-Raman.

Floresan Özellikli Boya İçeren ZnO Nanokompozit Kopolimerlerin Elektrokimyasal Sentezi ve Karakterizasyonu

Özet. Floresans boya sınıfından olan BODIPY'nin (Boron dipirolmetilen) bilim insanları tarafından sentezi uğraştırıcı olmasına karşın floresan, iyon / molekül ve pH probları, sensörler, redoks aktif moleküller, metal şelatörler, hücresel görüntüleme, fotodinamik tedavi, ilaç teslim malzemeleri ve fotovoltaik uygulamalar ve enerji depolama gibi çok çeşitli uygulamalarda kullanılması ilgi çekici olmuştur. Öncelikle çalışmada sentezi zor ama çekici floresans aktif monomer başarı ile sentezlenmiştir. Sonra elektrokimyasal yöntem kullanılarak yenilikçi malzeme olan bir iletken kopolimer sentezlenmiştir. Elde edilen yarı iletken malzemenin dayanım, iletkenlik özelliklerini arttırmak için Zno nanopartikülleri kullanılarak yine bir potansiyostat yardımı ile nanokompozit sentezlenmiş ve varlığı SEM-EDX, AFM-Raman gibi ileri teknolojik cihazlarla tayin edilmiştir. ZnO gibi inorganik ve nano ölçekli bileşiklerin karakteristik pikleri geleneksel FT-IR cihazında parmak izi bölgesinde ve zayıf/orta gözlenmektedir. Buda bahsedilen bileşiklerin kızılötesi spektrometre ile nitel teşhisini zorlaştırmaktadır. Buna karşın Raman spektroskopisi hem ICP-MS gibi nispeten uğraştırıcı hem de FT-IR gibi karmaşık bir spektrum bölgesi olmadığından nano parçacıkların tayininde tercih edilmiştir.

Anahtar Kelimeler**:** İletken polimerler, Nanokompozit, AFM-Raman.

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1. INTRODUCTION

Boron-dipyromene, abbreviated as BODIPY, is a class of fluorescent dyes. BODIPY is a powerful electron acceptor and has unique spectroscopic and photophysical properties such as high absorption rate and high fluorescence quantum yield and strong absorption in the visible region [1-3]. The BODIPY group exhibits adjustable redox potentials [4]. The photonic properties of BODIPY can be modifiable by functionalizing with donor molecules in meso- and pyrolytic positions (positions a and b). In this study, the meso position has been derivatized and the effect on redox behavior has been investigated by electrochemical method.

The synthesized BODIPY complex is made of conductive organic-inorganic nanocomposite polymer film due to its optoelectronic properties. Intense interest in conjugated polymers has been shown, depending on the wide range of applications where they are potentially useful since the discovery of the conductivity properties of polyacetylene [5]. Photovoltaic devices [6], light emitting diodes [7], field-effect transistors [8], electrochromic devices [9], and various sensors based on conjugated polymers [10] are being investigated by a large number of researchers worldwide. In this way, the search for new functional and sensitive conjugated polymers that exhibit electrochromism [11], photochromism [12] or non-linear optical properties, is particularly sought for applications in imaging technology or data storage. [13]. Organic-inorganic composites are a good candidate for many applications such as biosensing materials, bioanalytical application, organic optoelectronic device, gas sensor, carbon nanotube, and solar cells [2]. A polymer synthesis which has a combination of several of these properties has been targeted in this study.

Electropolymerization is a versatile method for producing electrically conductive polymers due to its simplicity and repeatability. It also allows the control of the thickness of the polymer film. Generally, electrical, optical and magnetic properties of conductive polymers, zinc oxide (ZnO), titanium oxide (TiO_2), cadmium sulfide (CdS), cadmium selenite (CdSe) and metal nanostructures etc. such as may be modified by the inclusion of inorganic materials. These inorganic materials include ZnO, wide band spacing (3,37 eV), large excitation bonding energy (60 meV), good chemical stability, interesting electrical and optical properties, and so on. It is well known for its outstanding features. Therefore, the development of ZnO / polymer nanocomposites for electrochromic device application is of great importance. Recently, ZnO-PEDOT-based nanocomposites have attracted considerable attention of material scientists in the field of optoelectronics, sensors and biomedical applications [14-17]. In this study, ZnO-PEDOT:BODIPY conductive nanocomposite copolymer film, which is an innovative material using electrochemical method, has been synthesized and characterized by advanced technologic devices such as NMR, SEM-EDX, AFM-Raman.

2. MATERIALS AND METHODS

2.1. Materials and instruments

Trifluoroacetic acid (TFA) and bortrifluoroetherate ($BF_3.OEt_2$) All other chemicals from Fluka were obtained from SigmaAldrich. Pirol was purified by filtration through an alumina-filled column prior to use. The monomers were chromatographed using 60 mesh silica using dichloromethane (DCM) as the starting phase. Polymerization Pt plate as the working electrode, Pt wire as opposite electrode and Ag / AgCl as the reference electrode were synthesized in CHI 600 potentiostat and 0.1M $LiClO_4$ / CH_3CN elektrolit pair in Niğde Ömer Halisdemir University Chemistry Department. For characterization, Scanning Electron Microscope (SEM-EDX) in Niğde Ömer Halisdemir University Central Research Laboratory Zeiss Evo 40, Ametek EDAX, Atomic Force Microscopy (AFM) Bruker Innova, RAMAN Renishaw Invia, Fourier Transformed Infrared Spectroscopy Bruker Vertex 70 instruments were used.

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2.2. Synthesis

BODIPY containing monomer containing fluorescence was synthesized according to literature [4-6] as shown in Figure 1. An aldehyde derivative (335 mg, 1.5mmol) was collected in a 100 mL single-necked flask. 50 mL of dry THF was added and N_2 gas was passed through the medium for 20 minutes. Pyrol (200 mg, 3 mmol) was added. After stirring for five minutes, TFA (three drops) was added and allowed to stir under N 2 gas at room temperature until the starting material ran out (2 days). The starting material was checked by thin layer chromatography (TLC). When the starting material was finished, DDQ (284 mg 1.25 mmol) was dissolved in 20 mL dry THF and transferred to the dropping funnel and added slowly to the reaction medium. Dry Et_3N (3.63 g, 5 mL, 35 mmol) and then $BF_3.OEt_2$ (3.45 g, 3 mL, 24 mmol) were added after 30 min. After stirring at room temperature overnight, the solvent was removed under reduced pressure. After determination of hexane / dichloromethane (1/1) mixture and dichloromethane as column solvent, the material was purified by column chromatography.

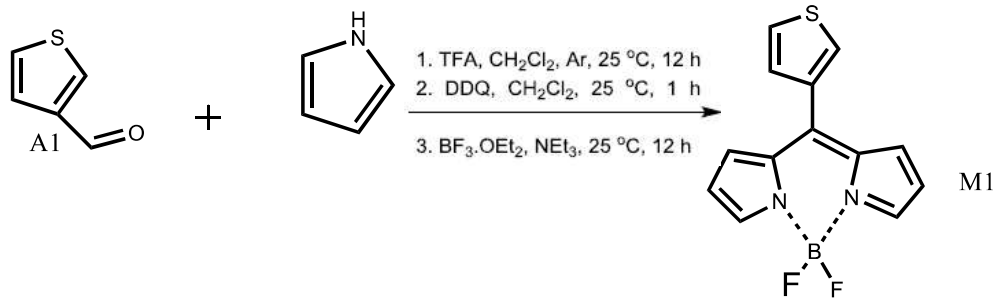


Figure 1. Synthesis scheme of M1 monomers.

2.2.1. 3-(4,4-difluoro-4-bora-3a,4a-diaza-s-indacene)-10-propyl-10H-thiophene (M1)

Thiophene 3-carboxialdehyde FT-IR spectrum in the 1700.72 cm^{-1} with the strong carbonyl peak stress, 2955 cm^{-1} aldehyde hydrogen stress is lost as a result of the reaction. 1610.98 cm^{-1} also proves the dimerization of pyrrole rings. FT-IR(cm^{-1}): 3471, 3060, 2970, 2128, 1610, 1514, 1574;^{1}H NMR (400 MHz, $CDCl_3$) d/ppm: 7.19 (d, J ¼ 8.7 Hz, 2H), 7.08 (d, J ¼ 8.7 Hz, 2H), 4.77 (d, J ¼ 2.37 Hz, 2H, OCH2), 2.57 (t, J ¼ 2.37 Hz, 1H, CH), 2.54 (s, 6H), 2.30 (q, J ¼ 7.57 Hz, 4H), 1.32 (s, 6H), 0.98 (t, J ¼ 7.57 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) d/ppm: 158.0, 153.5, 139.8, 138.3, 132.6, 131.1, 129.4, 128.9, 115.6, 78.0, 75.9, 56.1, 17.1, 14.7, 12.4, 11.9

2.2.2. Electrochemical polymerization of M1

Electropolymerization of monomers; Aggregate voltammetry using 20 mL 0.1M $LiClO_4$ as electrolyte in three-electrode electrochemical cells in which the P wire is used as the reference electrode, the platinum wire as the opposite electrode and the working electrode is separately Pt plate and the conductive and transparent indium tin oxide (ITO) coated glass surface is used. method. Copolymer synthesis was performed by adding 10ophl of EDOT (3,4-Ethylenedioxythiophene) to strengthen the electrochromic properties and to coat the film. The nanocomposite copolymer film was finalized by adding ZnO.

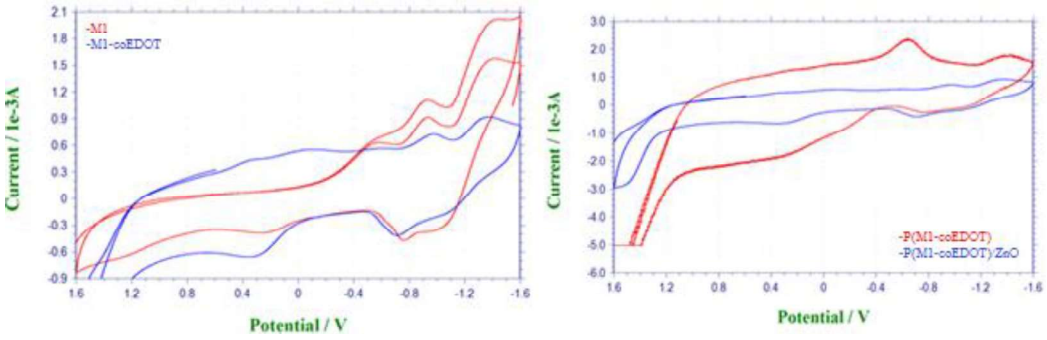


Figure 2. Cyclic voltamograms of M1, P (M1-coEDOT) and P (M1-coEDOT) / ZnO.

Table 1. Reduction and oxidation peak potentials of P(M1-co-EDOT), PEDOT, P(M1-co-EDOT)/ZnO, P-M1.

Product	Reduction Peak Potential (V)	Oxidation Peak Potential (V)
P(M1-co-EDOT)	-0.96, -1.35, -0.70	0.3, 1.5, 1.2, 0.4
PEDOT	-0.76	0.4
P(M1-co-EDOT)/ZnO	-0.65, -1.40, - 0.8	0.4, 0.96
P-M1	-0.56, -0.72, -1.0, -1.56	0,58

2.2.3. AFM-Raman analysis of P(M1-coEDOT)/ZnO nanocomposite polymer film

Figure 3 shows the AFM-Raman spectrum of the P (M1-coEDOT) / ZnO nanocomposite polymer film.

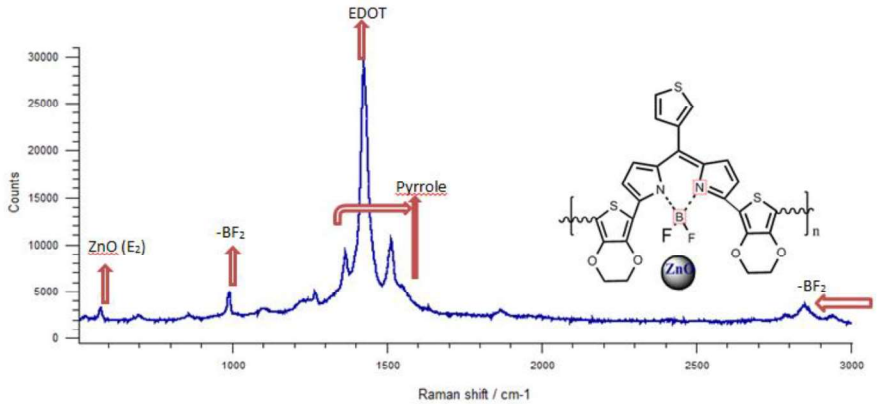
3. RESULT AND DISCUSSION

Thiophene 3-carboxialdehyde FT-IR spectrum in the 1700.72 cm^{-1} strong carbonyl peak tensile stress, 2955 cm^{-1} aldehyde in the reaction to the stress of the aldehyde lost. 1610.98 cm^{-1} also shows the dimerization of peak pyrrole rings.

In Figure 2, the cyclic voltamograms of monomer (M1), P- (M1-coEDOT) and P- (M1-coEDOT) / ZnO nanocomposite film are clearly different. Under the same conditions, the cathodic (reduction) and anodic (oxidation) peaks of EDOT are -0.76V and 0.4V as seen in Table1. The reduction and oxidation peaks of the P- (M1-coEDOT) copolymer are -0.96, -1.35, -0.70 and 0.3, 1.5, 1.2, 0.4 V, respectively, and are different from EDOT. This indicates that the copolymer was formed. In the literature, cathodic and anodic peaks belonging to ZnO are indicated as +0.106 and -0,06V [17]. The peak potentials of P- (M1-coEDOT) / ZnO nanocomposite film are given in Table 1. This difference is indicative of the nanocomposite polymer film.

The Raman shifts of ZnO nanoparticle in Figure 3 were observed at 100-400 cm^{-1} [7]. In the FT-IR spectra of the same substance, peaks correspond to the fingerprint area and make the determination difficult. At this point, Raman facilitates the determination of the trace and inorganic elements of the spectrum. The crystal structure of ZnO is hexagonal and has four atoms in the center (O-Zn-Zn-O). This four-member crystal lattice unit consists of 3n (n: member number), ie 12 lattice vibrations. 9 of these vibration movements are acoustic vibrations; 3 of them are optical vibrations. The highest vibration level called E2 was observed in Raman shift of 430 cm^{-1} [18]. Similarly, the observation of aromatic C = C raman shifts in the 1100 cm-1 and 1600 cm^{-1} range proves pyrrole and thiophene structures in the organic polymer film [3,8].

The result of the SEM-EDX with the AFM-Raman result of the copolymer nanocomposite film supports each other. As in the AFM-Raman data, SEM-EDX shows the peaks of Cα, S, N, Zn, O and Kα radiations in Figure 4. In the mapping, Zn dark green, O light green, N pink, C purple, S is represented by light purple colored speckles.



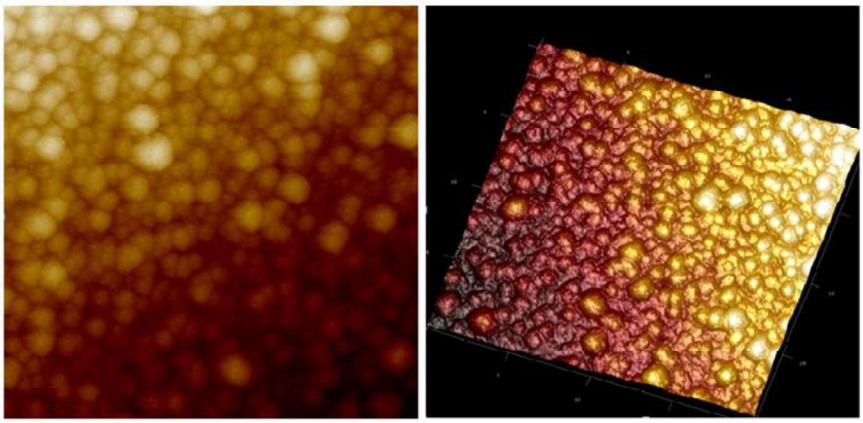


Figure 3. AFM-Raman spectrum of P(M1-coEDOT)/ZnO nanocomposite polymer film.

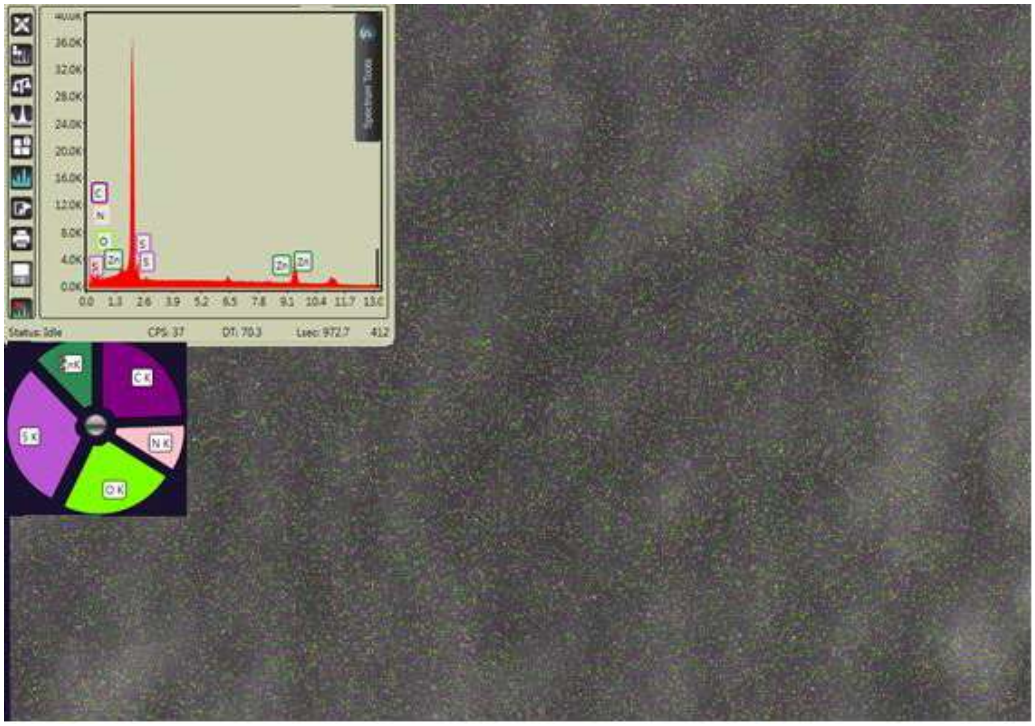


Figure 4. SEM-EDX analysis of P(M1-coEDOT)/ZnO nanocomposite polymer film.

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In this study, the promising BODIPY monomer synthesized, promising copolymer nanocomposite film has been successfully obtained and has been proven with new generation characterization devices in Niğde Ömer Halisdemir University Central Research laboratory.

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