

Preparation of Polyaniline/ZnO Films by Electrochemical Polymerization

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Abstract

A series of polyaniline (PANI)/zinc oxide (ZnO) nano-particle (diameter 70 nm) composite films were prepared by electrochemical polymerization in the presence of ZnO nanoparticle. Furthermore, PANI-ZnO/PVA (PVA = polyvinyl alcohol) double-layer system was prepared. We first report preparations of a photocatalyst/conducting polymer light absorber by using ZnO nano-particles.

Keywords

Light-Driven, Nano-Particle, Optical Activity

1. Introduction

Zinc oxide (ZnO) is well known as a photocatalytic inorganic material [1]. It has been investigated for applications in photocatalytic devices, photovoltaics, gas sensors, and piezoelectric energy harvesters [2]-[5]. ZnO has wide band gap (3.37 eV) and hole-electron binding energy of 60 mV [6]. ZnO can be used to collect high-energy photons (UV light) due to the large band gap. In order to expand its response range from UV light to visible light, employment of hetero-structure with narrow band gap semiconductors or dyes as sensitizers in combination with ZnO has been reported [6]-[8]. ZnO is a candidate for incorporation as a nano-particle within a polymer film.

Polyaniline (PANI) is one of the most remarkable conjugated polymers due to its relative ease of preparation in water solvent, environmental and thermal stability, and tunable conductivity [9]. Also, PANI thin films can be fabricated easily through various methods such as electrochemical polymerization, solution casting technique, and sol-gel spin coating [10]-[12]. It has promise for a large variety of applications, such as light emitting diodes, corrosion-inhibiting paint, and electro-chromic devices [13]-[15]. In previous research several reports focused

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on UV emission and photocatalytic activity of PANI/ZnO composite [6] [16]. Morphological changes in organic photoactive materials upon UV irradiation have been studied [17]-[19]. This paper reports preparation of optically active PANI/ZnO composite films, PANI-ZnO/polyvinyl alcohol double-layer films for application toward light-tunable devices.

2. Materials

Aniline (Wako, Japan) was first purified by distillation. (+)-Camphor sulfonic acid (Tokyo Chemical Industry (TCI), Japan), (-)-camphor sulfonic acid, sulfuric acid (TCI) and ammonium peroxodisulfate (APS, Kanto Chemical, Japan), zinc oxide nano-particles of diameter 70 nm were used as received.

3. Synthesis

3.1. PANI (CSA)-ZnO Composite

Electrochemical polymerization in the presence of ZnO nano-particles was performed to produce PANI (CSA)-ZnO composites, Films 1 (b-d) and 2 (b-d). An electrolyte was prepared by addition of the aniline and (+)-camphor sulfonic acid (or (-)-camphor sulfonic acid) as chiral dopants and nano-ZnO particles to distilled water (**Table 1**). Polymerization was performed by applying direct voltage (DC) at 3.0 V. Then, the resultant film was washed with distilled water and methanol to remove low molecular weight fractions and residual ZnO on the surface. The structure is illustrated in **Figure 1(a)**.

PANI doped with CSA film (Films 1a and 2a) without ZnO was prepared with the same procedure as preparation of Films 1 (b-d) and 2 (b-d).

3.2. PANI (CSA)-ZnO/PVA Layer (Double-Layer)

Electrochemical polymerization in without ZnO nano-particles was performed. The resultant film was immersed into a solution of dispersed ZnO in water/PVA (PVA = polyvinyl alcohol) producing a film with double-layer structure consisting of PANI (CSA) and ZnO/PVA.

First, chiral-PANI films were prepared on the anode side of ITO glass electrodes by electrochemical polymerization with no ZnO electrolyte solution. ZnO was dispersed in 0.1 wt% PVA solution. Here, PVA is employed as a matrix for ZnO. Then, the film was immersed into the dispersion. After drying, the chiral-PANI/ZnO double-layer film (Film 3a and 3b) was obtained. Washing was performed with the same procedure as preparation of Films 1(a-d). The structure is indicated in **Figure 1**.

Table 1. Preparation of PANI/ZnO and PANI-ZnO/PVA films.

Category	Film	Electrolyte solution				
		CSA ^a	H ₂ O (mL)	Aniline (mg)	ZnO (mg)	ZnO conc ^d /PVA in water soln ^e (M)
PANI/ZnO composite	Film 1b^b		1	20	4	
	Film 2b^b		1	20	4	
	Film 1c^b		1	20	12	
	Film 2c^b		1	20	12	
	Film 1d^b		1	20	18	
	Film 2d^b		1	20	18	
PANI-ZnO/PVA (double-layer)	Film 3a^c		1	20		0.06
	Film 3b^c		1	20		0.006

a) Camphor sulfonic acid (CSA). (+) and (-) represent optical activities. b), c) Abbreviations "1" and "2" correspond to (+)-CSA and (-)-CSA employed in the electrochemical polymerization, respectively. b) Electrochemical polymerization in the presence of ZnO nano-particles. c) Electrochemical polymerization with no ZnO nano-particles. Resultant films were immersed in the ZnO dispersed PVA in the water solution to deposit ZnO/PVA layer on the surface of the optically active PANI films. PVA = polyvinyl alcohol. d) Concentration of ZnO dispersion solution for immersion of PANI films. e) Dispersion concentration in 0.1 wt% PVA/water solution (M).

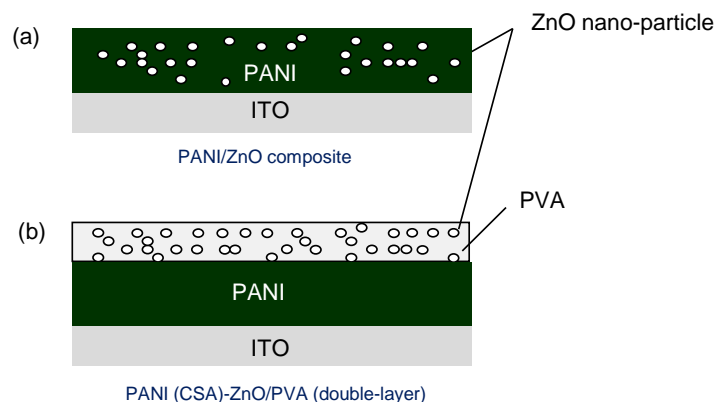


Figure 1. (a) PANI (CSA)-ZnO composite; (b) double-layer consisting of PANI (CSA) and ZnO/PVA layers. PANI = polyaniline, PVA = polyvinyl alcohol, CSA = optically active (+) or (-)-camphor sulfonic acid.

4. Results and Discussion

4.1. Optical Spectroscopy

Circular dichroism (CD) absorption spectroscopy measurements of the films were carried out to confirm optical activity. All of the films show Cotton effect in the CD. The signal intensities increase with increase of composition of ZnO in the PANI. Especially, Film 1d and Film 2d display clear and intense complementary mirror-image Cotton effect, shown in **Figure 2**. These films show intense CD signals compared with those of pure optically active polyanilines. This can be due to interaction between ZnO and the optically active main-chain (PANI-CSA) that amplify the chirality. Addition of large amounts of ZnO is required in the polymerization reaction because the resultant composite films cannot absorb all of the ZnO in the electrochemical polymerization. In other words, the yielding percentage of nano-ZnO in the PANI/ZnO composite can be low.

These film show optical absorption bands at 430 nm and at around 850 nm due to π - π^* transition of benzenoid segments and formation of polarons in quinoid segments respectively [20].

As for PANI-ZnO/PVA (Films 3a and 3b, double-layer film), an interface oxidation reaction between PANI and ZnO/PVA layers may occur; however, interfacial contact between ZnO and PANI via the PVA matrix may be low. So, photocatalytic doping of PANI with ZnO could not occur upon irradiation of UV light in this study.

4.2. Morphology and EDS

Scanning electron microscopy (SEM) images for Film 1d, 3a, and 3b are shown in **Figure 3**. In general, PANI-doped with CSA films show interconnected networks [21]. The films thus prepared display characteristic morphologies. Energy-dispersive X-ray spectroscopy (EDS) measurement result for Film 3a confirms the form of the film surface, because Film 3a has large amounts of Zn from ZnO (39.77 counts (a.u) in the component, **Table 2**). The EDS reveals that Film 1d contains small amounts of ZnO. This result implies that the PANI incorporates a small amount of ZnO during the electrochemical polymerization process.

4.3. IR

The FTIR spectra of Film 2a after UV irradiation in water were recorded as shown in **Figure 4**. The incorporation of CSA into the polyaniline chain was confirmed with FTIR. The characteristic IR absorption peak at 1574, 1497, 1302, 1249, 1148, and 817 cm^{-1} were found in all the spectra. These peaks are attributed to quinonoid (Q) C = C stretching, benzenoid (B) C = C stretching, ν_{QBQ} C-N stretching, ν_{BBB} C-N stretching, aromatic C-H in plane bending vibration, and C-H out-of-plane bending vibration of PANI, respectively [21]. Protonated polymer was confirmed with the peak at 1734 cm^{-1} (C = O stretching vibration) and 1047 cm^{-1} (SO_3^- vibration) derived from CSA. Spectra of the PANI layer are not changed upon the UV irradiation, indicating that the chemical structure of the PANI is not changed upon UV light irradiation.

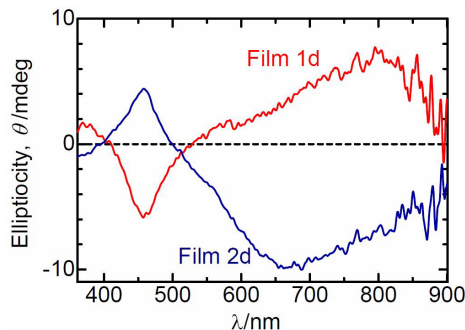


Figure 2. CD spectra of Film 1d and 2d.

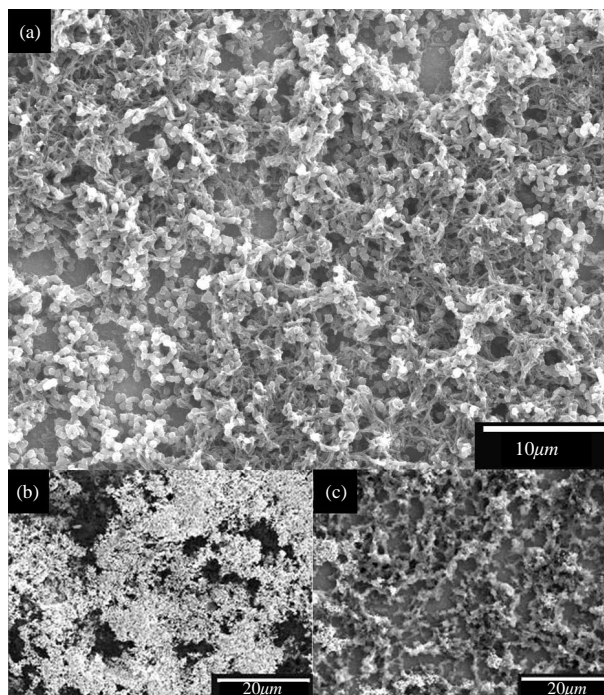


Figure 3. Scanning electron microscopy (SEM) images. (a) Film 1d; (b) Film 3a; (c) Film 3b.

Table 2. Energy dispersive X-ray spectroscopy (EDS) analysis for PANI/ZnO and PANI (CSA).

Film	C	N	O	S	Zn
	Counts (arb. units)				
Film 1d	51.45	24.30	19.91	3.39	0.96
Film 3a	36.87	3.01	19	1.36	39.77

4.4. Thermography

Figure 5 shows thermographic images of Film 3b on the ITO substrate upon infrared (IR, left) and ultraviolet (UV, right) light irradiation. The thermographic image upon irradiation of the IR light demonstrates that the film (Film 3b) absorbs visible range light and surface temperature is increased ($\Delta T = +5^{\circ}\text{C}$). On the other hand, the film absorbs UV light upon irradiation of UV light, and the surface does not reflect UV light, resulting no change of the surface temperature ($\Delta T = -5^{\circ}\text{C}$), although surrounding temperature is increased. PANI absorbs both the IR and the UV ranges, and ZnO absorbs UV light. So, ZnO enhances absorption of the UV light for the film.

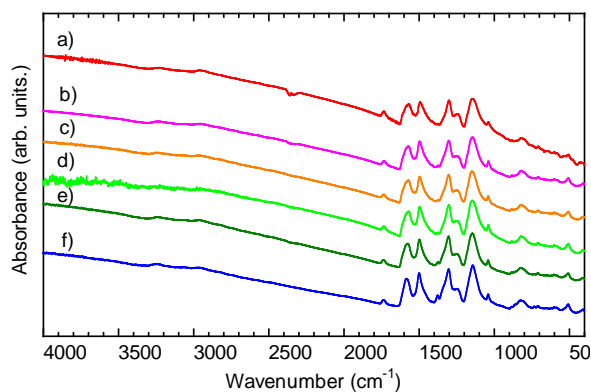


Figure 4. Fourier transform infrared (FTIR) spectra of Film 2a after UV irradiation. UV irradiation time is 0 min (a), 0.5 min (b), 1 min (c), 3 min (d), 5 min (e), and 10 min (f).

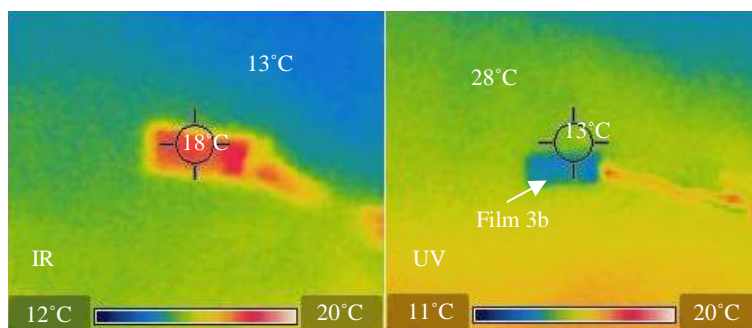


Figure 5. Themographies of Film 3b upon IR (left) and UV (right) irradiation.

5. Conclusion

We prepared PANI/ZnO composites by electrochemical polymerization and PANI-ZnO/PVA double-layer systems with electrochemical polymerization followed by immersion in ZnO/PVA water solution. Chemical polymerization of PANI in the presence of ZnO to prepare PANI/ZnO nanocomposites was carried out in previous work [22]. The combination demonstrates the ability of producing photocatalyst/conducting polymer thin films. Future research should pursue improvement of the interaction between PANI and ZnO nano-particles in the polymerization to obtain PANI incorporating larger amounts of ZnO.

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Techniques

Ultraviolet and visible (UV-vis) spectroscopy was recorded on a JASCO V-630 spectrophotometer. Circular dichroism (CD) spectroscopy was recorded on a JASCO J-720 spectrometer. An artifact detection/offset system was used for the measurements. Scanning electron microscopy (SEM) observations and energy-dispersive X-ray spectroscopy (EDS) were carried out by a JEOL JSM-7000F and JED-2200. Infrared (IR) absorption spectra were obtained using a Thermo Scientific NICOLET iS5 with the KBr method. Electron-spin-resonance (ESR) measurements were performed with a Bruker EMX-T ESR spectrometer. Thermographic images of the films

were obtained with an FLIR i5 (FLIR Systems).

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