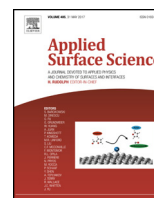




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Full Length Article

Conductivity enhancement of surface-polymerized polyaniline films via control of processing conditions

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ABSTRACT

We investigate a fast and facile approach for the simultaneous synthesis and coating of conducting polyaniline (PANI) onto a substrate and the effects of processing conditions on the electrical properties of the fabricated films. Simultaneous polymerizing and depositing on the substrate forms a thin film with the average thickness of 300 nm and sheet resistance of 304 Ω /sq. Deposition conditions such as polymerization time (3–240 min), temperature (-10 to 40 °C), concentrations of monomer and oxidant (0.1–0.9 M), and type of washing solvents (acetone, water, and/or HCl solution) affect the film thickness, doping state, absorption characteristics, and solid-state nanoscale morphology, therefore affecting the electrical conductivity. Among the conditions, the surface-polymerized PANI film deposited at room temperature with acetone washing showed the highest conductivity of 22.2 S/cm.

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1. Introduction

Conducting polymers have attracted significant attention for potential uses in novel applications, because they offer good electrical properties, low-cost processing, and mechanical flexibility [1]. Among the conducting polymers, polyaniline (PANI) has been particularly widely studied because of its simple synthesis in ambient air conditions and easy control of doping levels that allows adjustment of the electrical conductivity. PANI has been applied in thin-film transistors, light-emitting diodes, solar cells, batteries, and supercapacitors [2–4].

Various synthesis methods for PANI have been studied, including emulsion [5], solid/liquid interfacial [6], liquid/liquid interfacial [7], seeding [8], enzymatic [9], mechanochemical [10], template-guided [11], and sonochemical techniques [12]. However, most bulk-synthesized PANI specimens show low solubility in common solvents, hindering processability. In other words, the combination of emulsion polymerization and spin-coating often fails to exploit the processability of polymers because of the lack of good solvents, other than toxic chemicals such as *n*-methyl-2-pyrrolidone (NMP) and *m*-cresol. To overcome this issue, various dopants and processing agents have been studied in order to improve the processability of PANI [13]. Alternatively, methods of direct coating such as in-situ polymerization [14–16] and interfacial polymerization [7] have

also been developed. A new and convenient method that decreases the effort of synthesizing and processing thin-film PANI must be found.

Herein, we demonstrate a fast and facile method of simultaneous synthesis and coating of PANI films on ambient surfaces with nanoscale film thickness and improved electrical conductivity. The presented method of PANI deposition provides an alternative coating technology expected to facilitate the formation of conductive films on surfaces of various materials and geometries. Through systematic investigation, we also found that the doping state and electrical properties of surface-polymerized PANI are affected by the processing conditions. An electrical conductivity reaching 22.2 S/cm obtained from our processing exceeds that reported in a related work of sub-micrometer-thick films formed by in-situ polymerization in the presence of hydrochloric acid (~ 7 S/cm) [17]. Since PANI morphology and conductivity have been reported to correlate closely [18], we also trace changes in the spectroscopic features and solid-state morphology of the films as functions of the processing conditions, and correlate these changes with the electrical properties.

2. Experimental section

2.1. Materials

Aniline, ammonium peroxydisulfate (APS), and aqueous hydrochloric acid solution (1 M of HCl in H₂O) were obtained from Sigma-Aldrich. All chemicals were used without any purification.

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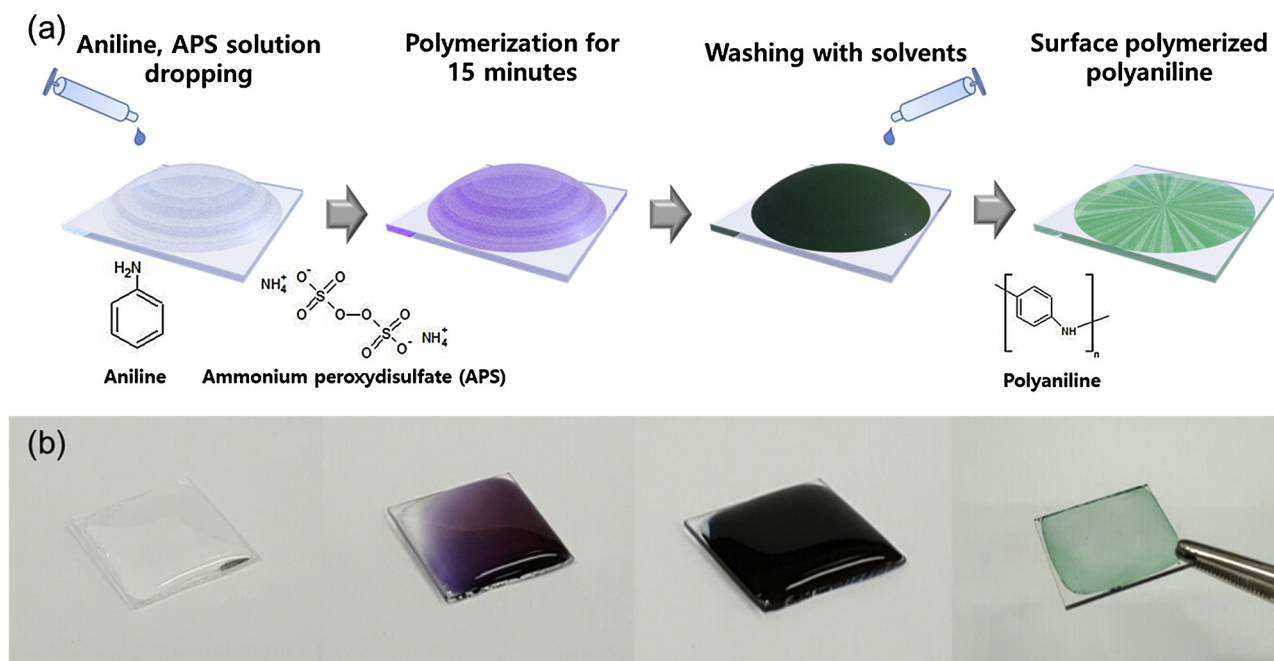


Fig. 1. (a) Schematic of the PANI synthesis procedure. (b) Digital photographic images of samples during polymerization and the resulting PANI film.

Pieces of microscope slide glass (Marienfeld-Superior) were used as substrates for PANI deposition.

2.2. Surface polymerization of PANI

Aniline solution and APS solution were prepared with various molar concentrations (0.1 M, 0.3 M, 0.5 M, 0.6 M, 0.7 M, and 0.9 M) in a solution of 1-M HCl. In this work, we named the PANI films as SP_xy, where *x* describes the first digit of the aniline concentration (e.g., $x \times 10^{-1}$ M) and *y* describes that of the APS concentration (e.g., $y \times 10^{-1}$ M). The glass substrates were cleaned by sequential sonication in deionized (DI) water, acetone, and isopropyl alcohol for 10 min each before drying under flowing N₂ and holding in ambient atmosphere for at least 3 h. Onto a clean glass substrate (1.5 cm × 1.5 cm), 0.3 mL of the aniline solution was cast, and then 0.1 mL of the APS solution was carefully added on top of the aniline droplet. Polymerization was performed at room temperature for 15 min or a controlled period of time, after which the leftover APS solution droplet was washed away by a flow of various solvents (acetone, DI water, or 1-M HCl solution) or a sequential application of these solvents. For the study of temperature dependence, we prepared PANI in a temperature-controlled chamber. The films were dried in a vacuum oven for 24 h or annealed at 150 °C for 10 min. For ultraviolet–visible (UV–vis) absorption measurements, 0.6 mL of the aniline solution and 0.2 mL of the APS solution were dropped onto a larger glass substrate (2.5 cm × 2.5 cm).

2.3. Characterization

Fourier-transform infrared (FT-IR) spectra of surface-polymerized PANI were obtained from PANI samples deposited on a silicon wafer substrate using an FT/IR-4700 spectrophotometer (JASCO, Inc.) over the wavenumber range of 4000–400 cm⁻¹. UV–vis spectra were obtained from PANI samples on a glass substrate using a V-670 spectrophotometer (JASCO, Inc.) in the range of 300–1000 nm. The PANI nanostructures were imaged with a field-emission scanning electron microscope (FE-SEM). The sheet resistance (*R_s*) was measured using an in-line four-point-probe

resistivity meter. The electrical conductivity σ was calculated from the thickness (*t*) and *R_s* using the following equation: $\sigma = 1/(R_s \times t)$.

3. Results and discussion

3.1. Visual observation in surface polymerization of PANI

For the simultaneous synthesis and deposition of polyaniline (PANI), we dropped the aniline solution onto a substrate and then added the ammonium peroxydisulfate (APS) solution (Fig. 1). Because both chemicals are dissolved in a solution of hydrochloric acid (HCl), acid doping of PANI also occurred. The synthesis and doping of PANI can be easily detected from the color change of aniline in acidic conditions when in contact with APS. A colorless droplet of the aniline solution initially turns violet and then dark green within several minutes, indicating polymerization and doping to form PANI emeraldine salt. We applied our proposed approach to various hydrophobic substrates, including polyimide adhesive tape, polydimethylsiloxane elastomer, octylsilane-treated silicon dioxide, a polystyrene dish, 3 M tape, and polyethylene terephthalate transparency films. The method was successful on relatively hydrophobic substrates. With hydrophilic surfaces, the washing solvent penetrates the interface between the PANI film and substrate, causing film peel-off from the substrate during the washing procedure.

3.2. Spectroscopic analyses

We investigated the FT-IR and UV–vis spectra in order to verify the successful formation of the proper chemical bonds and optical transitions in the PANI films synthesized through the surface polymerization method (Fig. 2). Fig. 2(a) shows the FT-IR spectra of the SP₆₆ samples (surface-polymerized samples made using 0.6-M aniline and 0.6-M APS) after drying in different conditions. We confirm that the deposited film is indeed doped PANI based on FT-IR spectral peak assignment. Two peaks at 1490 and 1573 cm⁻¹ indicate the benzenoid and quinoid rings present in doped PANI. The C–N bonding peak of aromatic amine is seen at 1319 cm⁻¹. The peaks of C–H aromatic ring bonding are located at 1129 and 802 cm⁻¹.

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