



# Fabrication of honeycomb-patterned polyaniline composite films using chemically modified polyaniline nanoparticles



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## ABSTRACT

A novel polyaniline composite was prepared by in situ ring-opening polymerization of  $\epsilon$ -caprolactone in the presence of chemically modified polyaniline nanoparticles (PANI-NPs) using  $\text{Sn}(\text{Oct})_2$  as an initiator, which exhibited a high solubility in organic solvent to enable the fabrication of stable honeycomb-patterned thin films by casting the PANI composite solutions under humid conditions. The chemically modified PANI-NPs were produced from the polymerization of aniline in the cationic surfactant of cetyl trimethyl ammonium bromide (CTAB). The polyaniline composites were characterized via Fourier transform infrared, ultraviolet–visible spectroscopy, X-ray diffraction, transmission electron microscopy, and thermogravimetry. The analyses indicated that the PANI-NPs were well incorporated in the poly( $\epsilon$ -caprolactone) (PCL) backbone. The patterned PANI composite films showed high DC conductivity up to  $10^{-2}$  S/cm, which can be useful in applications such as bio-sensing, bio-nanotechnology, biological science, and medicine.

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## 1. Introduction

Intrinsically conducting polymers (ICPs) have received considerable attention because of their outstanding electronic, electrochemical, and optical properties, as well as their facile polymerization and low cost [1,2]. Among the various conducting polymers, polyaniline (PANI) is frequently investigated because of its numerous applications, such as in electrochromic devices and/or energy storage [3–8], antistatics, charge dissipation and electrostatic dispersive (ESD) coatings and blends, electromagnetic interference shielding (EMI), anti-corrosive coatings [9,10], hole injection layers [11], transparent conductors, ITO replacements [12,13], actuators, chemical vapor- and solution-based sensors [14,15], PEDOT-PSS replacements, toxic metal recovery, catalysis, as well as fuel cells and active electronic components [11,16].

However, insolubility in common organic solvents and infusibility at melt-processing temperatures are the major disadvantages of PANI. These disadvantages are associated with the stiffness of the PANI backbone and the hydrogen-bonding interactions between the imine and amino groups [17]. Various approaches have been applied to improve the solubility and processability of PANI.

Among these methods, covalent substitutions, such as ring substitution [18–20] and copolymerization of an aniline monomer and an appropriate monomer [21–23], as well as protonation with functionalized protonic acids, such as dodecylbenzenesulfonic acid [24] and camphorsulfonic acid [25], have been well investigated. Nanometer-scale dispersible PANI particles have also drawn much attention because of their special physical and chemical properties [26–29].

Honeycomb-patterned thin polymer films are eliciting attention because of their potential application in various fields, such as separation membranes, super hydrophobic materials, photonic and optoelectronic devices, cell-culturing substrates, and micro-patterning templates [30,31]. These films are fabricated by various methods, such as lithography, use of colloidal crystals, self-assembly and rod-coiled copolymers [32,33]. The breath-figure method is a simple and useful fabrication method for these films [34–37]. In this method, the substrate is completely dispersed in organic solvents, such as chloroform, and the films are subsequently fabricated by casting these solutions under humid conditions.

Honeycomb-patterned thin films of conducting polymers and their composites have great potential applications. Specifically, patterned conducting polymer films with honeycomb structures can improve the performance of sensing devices because their porous structures provide relatively high active surface areas for

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detections [38–40], and they can also improve the performance of solar cells and solar cell applications because of the light scattering in the internal structure of the film [41–43]. In biological systems, the honeycomb-patterned films of conducting polymers provide a convenient approach to modify and functionalize neural electrodes because of their inherent electrical conductivity and ease of fabrication on electrode surfaces. The high surface areas available with porous structures facilitate ion exchange between the electrodes and surrounding tissues [44,45]. The electrical current stimulation of biological systems benefits the growth of cells [46]. Honeycomb structures can improve interaction between PANI with amino acids, proteins, enzymes, and living cells in its patterned films, as well as serve as a surface for tissue engineering [47].

Therefore, the methods for the fabrication of honeycomb-patterned PANI porous thin films have raised considerable interest. Various approaches have been used to fabricate PANI honeycomb-patterned films [48–50]. However, the poor solubility of PANI in organic solvents has limited the easy fabrication of honeycomb-patterned porous PANI films [48].

Poly( $\epsilon$ -caprolactone) (PCL), a biodegradable and biocompatible polyester, has drawn considerable attention from both academic and industrial fields [51,52]. PCL is a suitable material for forming composites with functional materials, including conductive materials, through *in situ* polymerization of  $\epsilon$ -caprolactone in the presence of functional components. PCL has numerous potential applications, such as in biomedical materials, biomedical engineering, biosensors and microparticles for drug delivery [53–55].

In this study, organic soluble PANI-NPs were synthesized through the polymerization of aniline monomer in a micellar solution containing a cationic surfactant. A novel, organic solvent-soluble PANI composite was synthesized through *in situ* ring-opening polymerization of  $\epsilon$ -caprolactone in the presence of PANI-NPs. The incorporation of PANI-NPs into the PCL chains transformed the PANI into chloroform-soluble composites, enabling the fabrication of porous honeycomb-patterned thin films through casting of the composite solutions under humid conditions. The spectral characteristics, thermal behavior, and morphology of the PANI-NPs and those of the composite were investigated. The pattern structure and DC conductivity of the honeycomb-patterned PANI composite films were studied.

## 2. Materials and methods

### 2.1. Materials

$\epsilon$ -Caprolactone (99% purity, Aldrich) was purified through recrystallization using absolute methanol, and was dried in vacuum at 30 °C. Aniline monomer (reagent grade, Aldrich) was distilled under vacuum and subsequently stored in a dark recipient at low temperature prior to use. Analytical-grade cetyl trimethyl ammonium bromide (CTAB), ammonium persulfate (APS, 99%), concentrated HCl, benzyl alcohol, tin octoate ( $\text{Sn}(\text{Oct})_2$ ), toluene, methanol, acetone, and chloroform were used as-received from Aldrich Co. Deionized water was used in all of the experiments.

### 2.2. Experimental details

#### 2.2.1. Synthesis of PANI-NPs

PANI-NPs were synthesized through chemical oxidative polymerization of aniline in an aqueous solution containing CTAB. A total of 90 mmol of CTAB was added to 100 mL of 1 M HCl aqueous solution, and the resulting mixture was vigorously stirred at room temperature for 20 min before adding 30 mmol of aniline. Then, 5 mL of 1 M HCl aqueous solution containing 30 mmol of APS

$(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) was slowly added and stirred in an ice bath at 0 °C–4 °C for 24 h. Before adding the initiator solution, the micelle morphology of mixture of aniline monomer and CTAB was measured by small angle X-ray scattering (SAXS) (Nano STAR, Bruker AXS Co.). The precipitate was mixed with an excess of methanol, filtered, and washed with distilled water and acetone. PANI homopolymer was synthesized in bulk aqueous solution without CTAB under the same conditions to compare it with the PANI-NPs.

#### 2.2.2. Synthesis of polyaniline composites

The procedure for the synthesis of PANI composites is similar to the formation of a composite introduced in our previous report [56]. A total amount of 10 g, including predetermined percentages of PANI-NPs and  $\epsilon$ -caprolactone, was placed in a flask containing 30 mL of toluene. This mixture was sonicated at room temperature for 1 h. The mixture reaction was conducted at 80 °C for 36 h in the presence of  $\text{Sn}(\text{Oct})_2$  (0.1 g, 1 wt % of the monomer) as a catalytic agent and benzyl alcohol (0.015 g) as a co-initiator under nitrogen atmosphere. The resulting polymer composites were dispersed in chloroform, precipitated in cold methanol, washed, and dried at 40 °C in vacuum. The percentages of PANI-NPs used during the polymerization of the PANI-PCL (PLANI) composites were 10, 20, 30, 40 wt%, and 50 wt% abbreviated as PLANI-10, PLANI-20, PLANI-30, PLANI-40, and PLANI-50 respectively. The same procedure was repeated to synthesize pure PCL homopolymer without the addition of PANI-NPs for comparison.

#### 2.2.3. Characterization

The PANI, PANI-NPs, PCL, and PLANI composite samples were pelletized with potassium bromide, and their infrared (IR) spectra were obtained using an FTIR spectrophotometer (Model 1600, Perkin–Elmer). Approximately 60 scans were signal-averaged with a resolution of 2  $\text{cm}^{-1}$  from 4000  $\text{cm}^{-1}$ –400  $\text{cm}^{-1}$ . The UV–vis spectra of the samples in chloroform were obtained using a Shimadzu UV–vis–NIR spectrophotometer (UV-3101PC). X-ray diffraction (XRD) patterns were obtained using a Rigaku D/MAX 2500 diffractometer with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at a generator voltage and current of 40 kV and 200 mA, respectively. Thermogravimetric analysis (TGA, Perkin Elmer TGA 7) was used to analyze the thermal properties at a heating rate of 10 °C  $\text{min}^{-1}$  under a nitrogen atmosphere.

#### 2.2.4. Fabrication of honeycomb-patterned PANI composite thin films

The procedure for the preparation of honeycomb-patterned polymer thin films was discussed in detail in our previous report [56]. Each solution containing 0.25 g of powder samples in 4 mL of chloroform was sonicated at room temperature for 1 h. Then, the solution was cast into a glass Petri dish at 25 °C under a relative humidity of 60%. Honeycomb-patterned films were formed by the condensation and deposition of water droplets on the solution surface through evaporative cooling [35–37]. The morphologies of the powder samples and the obtained patterned films were characterized via transmission electron microscope (TEM, JEOL model JEM-2010) and scanning electron microscopy (SEM, COXEM model CX-100). For the conductivity of the obtained composite films, DC conductivity was measured using the four-probe technique with a Keithley 224 constant current source and a Keithley 617 digital electrometer, and for the non-conductive PCL films, the surface resistivity was measured by the impedance analyzer (E4990A, Agilent Tech.). Fig. 1 shows the overall experimental scheme for the synthesis of PLANI composite and the fabrication of the honeycomb-patterned film.

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