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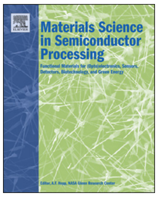

In situ deposition of polythiophene nanoparticles on flexible transparent films: Effect of the process conditions

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ABSTRACT

Polythiophene (PTh) was deposited as a thin film and nanoparticles on polyethylene naphthalate (PEN) films via ultrasonication or via magnetic stirring with or without a cationic (cetyltrimethylammonium bromide, CTAB) or non-ionic (Triton X-100) surfactant. The resulting conductive flexible films were characterized by UV-Vis spectroscopy, fluorescence spectrometry, field-emission scanning electron microscopy, contact angle measurements, the four-point-probe technique, X-ray diffraction, and cyclic voltammetry. The highest conductivity was obtained for PTh-CTAB nanoparticles, which had the most compact surface morphology among nanoparticles on PEN films. In general, the surface morphology, electrical conductivity, and whether PTh nanoparticles had been precipitated or deposited depended on the surfactant used, the surfactant/monomer ratio, the oxidant/monomer ratio, and the monomer concentration.

1. Introduction

One way to fulfill the requirements for better, faster, smaller, lighter, and more flexible electronic devices is to use polymeric materials for various device parts [1,2]. For instance, polyethylene naphthalate (PEN) has attracted attention for optoelectronic devices because of its flexibility, transparency, chemical inertness, dimensional and thermal stability, and solvent resistance, in addition to the possibility of mass production in roll-to-roll processes [2,3]. Conducting polymer (CP) thin films are currently used as transparent conducting electrodes in optoelectronic devices [1,2]. As a CP subclass, CP nanostructures not only retain the unique properties of CPs but also have nanomaterial characteristics such as size and quantum effects, a large surface area, and size-dependent optical, magnetic, electronic, and chemical properties [4,5]. Polythiophene (PTh) nanostructures are important materials because of their unique properties, including low production cost, large π-conjugated structure, high conductivity, and ease of synthesis [6].

Therefore, CPs are being considered as replacements for transparent anode electrodes such as indium tin oxide (ITO) and for flexible electronic devices (FEDs) including photovoltaic cells and organic light-emitting diodes (OLEDs). CPs overcome some of the disadvantages of ITO, such as the cost of indium, the toxicity of tin, the in-service lack of indium, weak interfacial compatibility with organic materials, and poor mechanical and chemical stability in FED applications [7–11]. CPs have been used in bulk heterojunction photovoltaic devices and exhibit suitable efficiency comparable to that of devices prepared using ITO [12,13]. CP thin films have also been used as transparent flexible electrodes in OLEDs with high quantum efficiency [14].

To date, hard and soft template methods, as well as approaches such as ultrasonication, have been used to synthesize CP nanostructures [4,15,16]. Template synthesis

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has been the main method for producing PTh nanostructures with a regular structure such as nanotubes and nanowires. However, removal of the template after nanosized PTh formation is an intrinsic problem and may damage the material structure [4,17]. Surfactants offer reliable media as soft templates and have been used to synthesize PTh nanostructures [4]. For instance, layered, ribbon-, and globular-like PTh nanostructures prepared using different cationic, anionic, and non-ionic surfactants as soft templates exhibited different morphology and electrical conductivity, depending on the surfactant [18,19]. Among results reported in the literature, PTh powder prepared using non-ionic surfactants (Triton X-100 or Tween 20) show higher electrical conductivity compared to materials prepared using anionic and cationic surfactants. Therefore, it can be concluded that the properties of the resulting PTh are greatly influenced by the nature of the surfactant in the polymerization solution [20–23].

Ultrasonication, usually in the frequency range from 20 kHz to 1 MHz, has been used to increase the rate of organic, inorganic, and polymerization reactions [24]. In the case of CPs, ultrasonically synthesized products have resulted in films with finer structural features and denser morphology [25,26]. Ultrasonication can enhance the diffusion rate of the monomer and other chemical species in solution via microagitation and/or cavitation effects, which minimize the formation of the diffusion layer. This enhanced mass transfer results in uniform deposition of the polymer film on the electrode [27,28].

To the best of our knowledge, there are no reports on chemical deposition of PTh nanoparticles on flexible polymeric substrates. Most of the studies on deposition of PTh nanostructures on substrates have involved electrochemical polymerization techniques [29].

In the present study we prepared conductive transparent flexible films via deposition of PTh nanoparticles on a polymeric transparent substrate. The product has potential for conducting transparent anode electrodes in photo- and opto-electronic devices such as flexible displays. Here we report on the electrical, physical, and morphological properties of PTh synthesized *in situ* and deposited under various reaction conditions, including ultrasonication or magnetic stirring in the presence or absence of a surfactant (cationic cetyltrimethylammonium bromide, CTAB, and non-ionic Triton X-100). PTh was synthesized *in situ* and deposited on PEN films in the form of film and nanoparticles for comparison. Desirable properties were obtained on PEN films modified using piranha solution and CTAB, so these conditions were used to investigate other reaction parameters. These included the oxidant/monomer molar ratio, the CTAB/monomer molar ratio, and the monomer concentration. We investigated the degree of polymer deposition, the morphology, and the electrical conductivity of the samples.

2. Experimental

2.1. Materials

PEN substrates (thickness 0.05 mm, biaxially oriented and semi-crystalline) were purchased from Goodfellow (UK). Thiophene monomer was purchased from Merck and was purified by distillation under reduced pressure and stored at 4 °C until use. CTAB, Triton X-100, acetonitrile (CH_3CN), anhydrous iron (III) chloride, methanol, iodine, sulfuric acid (95–98%), and hydrogen peroxide (30%) were purchased from Merck and were used as received without further purification.

2.2. PEN surface modification

PEN sheets were cut into pieces of 4.5 cm × 2 cm. These were washed with detergent and distilled water and then sonicated in acetone and dried with N_2 gas. The PEN surface was modified using piranha solution (mixture of 20 mL of 95–98% sulfuric acid and 10 mL of 30% hydrogen peroxide) at 65 °C for 30 min to improve the adhesion. This generates oxygen-containing functional groups on the PEN surface and leads to irregular surface etching according to our experiences [30]. After piranha treatment, the substrates were immediately immersed in distilled water for 5 min and then rinsed with plenty of distilled water and dried using N_2 gas.

2.3. Deposition of PTh films and nanoparticles

2.3.1. In situ deposition of PTh thin film under magnetic stirring

Thiophene (2.4 mmol, 0.19 mL) was mixed with acetonitrile (8 mL) as the monomer solution. One side of the PEN substrate was covered with adhesive tape and the sample was immersed in oxidant solution containing anhydrous $FeCl_3$ (12 mmol, 1.946 g) in acetonitrile (8 mL) for 20 min. Then the monomer solution was added dropwise to the oxidant solution. The mixture was constantly stirred for 24 h at 4 °C. The substrate was then removed from the polymerization solution and immersed in deionized water for 30 min to stop polymerization and remove unreacted materials and loosely bound oligomers. The sample was then sonicated in methanol, rinsed with acetone, and dried using N_2 gas. Iodine vapor was used to dope the PTh film in a closed vessel containing 100 mg of solid iodine at ambient temperature for 72 h.

2.3.2. In situ deposition of PTh nanoparticles in the presence of surfactants

Thiophene (2.4 mmol, 0.19 mL) was mixed with acetonitrile (4 mL) as the monomer solution. Surfactant (0.06 mmol of CTAB or Triton X-100) was dissolved in 4 mL of acetonitrile and added to the monomer solution and stirred for 30 min at 30 °C. The oxidant solution containing anhydrous $FeCl_3$ (12 mmol, 1.946 g) in acetonitrile (8 mL) was prepared separately. The other steps were the same as in Section 2.3.1.

2.3.3. In situ deposition of PTh nanoparticles under ultrasonication

The same procedure as in Section 2.3.1. was used but with ultrasonication instead of magnetic stirring. This involved sonication of the polymerization solution in an ultrasonic bath (Digital ultrasonic, CD-4820, 42 kHz, and 170 W) without surfactant for 10 min at 4 °C (ice-water bath). Purification, drying, and doping were as described