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Synthesis and electrochromic properties of conducting polymers: Polyaniline directly grown on fluorine-doped tin oxide substrate via hydrothermal techniques

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ABSTRACT

Inspired by hydrothermal synthesis of inorganic crystallites, we apply one-step hydrothermal polymerization to directly grow polyaniline on fluorine-doped tin oxide (FTO) substrate. In contrast to classical procedure that requires long reaction times and low temperature, hydrothermal polymerization allows for only 3 h under hydrothermal condition. Investigation of the morphology via SEM suggests that PANI fiber aggregates uniformly on FTO substrate. The PANI film was used as electrochromic layer in an electrochromic device and the obtained PANI film shows high electrochromic performance. We believe that this study provided a novel way to directly grow PANI on FTO substrate and, thus, has some impact on the applications of other conjugated polymers in electrochromic and electrochemical devices.

1. Introduction

Conjugated polymers have attracted widespread interest during the last two decades due to their unique electronic, optoelectronic and electrochemical properties [1,2]. Among this type of polymers, Polyaniline (PANI) has attracted special attention due to several reasons: it can be easily prepared by standard oxidation chemical or electrochemical polymerization; it demonstrates higher conductivity and environmental stability and it owns multicolor compared to other conducting polymers [3–5]. During the last three decades PANI became one of the most extensively studied conducting polymers. The different charges, colors and conformation of the multiple oxidation states make the PANI promising for applications in supercapacitors [6–9],sensors [10,11], electrochemical actuators [12], electrochromic devices [13–18] and fuel cells [19,20]. The classical syntheses of PANI are employing oxidative polymerization of aniline or electrochemical syntheses of PANI. PANI of high molecular weight is usually obtained as amorphous products, because they are more difficult to crystalize than small molecules. Little progress has been made in the last decades towards alternative polymerization techniques, e.g., aniline polymerization under X-ray irradiation [21], chemical oxidative polymerization of vaporized aniline monomer on inkjet-printed oxidant patterns [22] and polymerization of aniline in pulsed dc plasma [23]. In spite of the lots amount of reports focused on the choice of oxidants there are few examples of the synthesis focus on the synthesis conditions. For high-performance conducting polymers, nanostructures is a desired feature: it enhances mechanical and thermal strength, or directional properties such as electrical and optical properties. So there is increasing interest in environmental friendly routes to the synthesis of conducting PANI.

The synthesis of PANI can be done in a chemical method to control the growing process. One of the possible approaches to achieve the nanostructures is hydrothermal method. Our approach for the hydrothermal synthesis of PANI is inspired by nature. Hydrothermal method is widely used in the synthesis of inorganic materials, ranging from zeolite synthesis to the artificial crystals. Yet, only few examples exist for the synthesis of organic materials under hydrothermal conditions, mostly dealing with small organic molecules. Recently, several typical polymers synthesized by hydrothermal method have been reported. Zhu and coworkers prepared three polyaniline nanoarchitectures of square nanosheets, microsphere and microdisks using hydrothermal method in the presence of CTAB as a template [24]. Shi synthesized different PANI mesostructures under hydrothermal conditions [25]. Unterlass and coworkers developed highly ordered polyimides via hydrothermal polymerization [26]. The resulting polymer shows superior thermal stability and excellent crystallinity. Hydrothermal polymerization present a fascinating advantage to conventional method: they are carried out in a single step and originally green with water as solvent. Although the syntheses carried out in the water, the polymerization work very well and even lead to highly crystalline polymer. Therefore, hydrothermally-produced conducting PANI has the opportunity to be at the forefront of becoming novel and evolving polymeric materials under high-temperature aqueous solutions at high vapor

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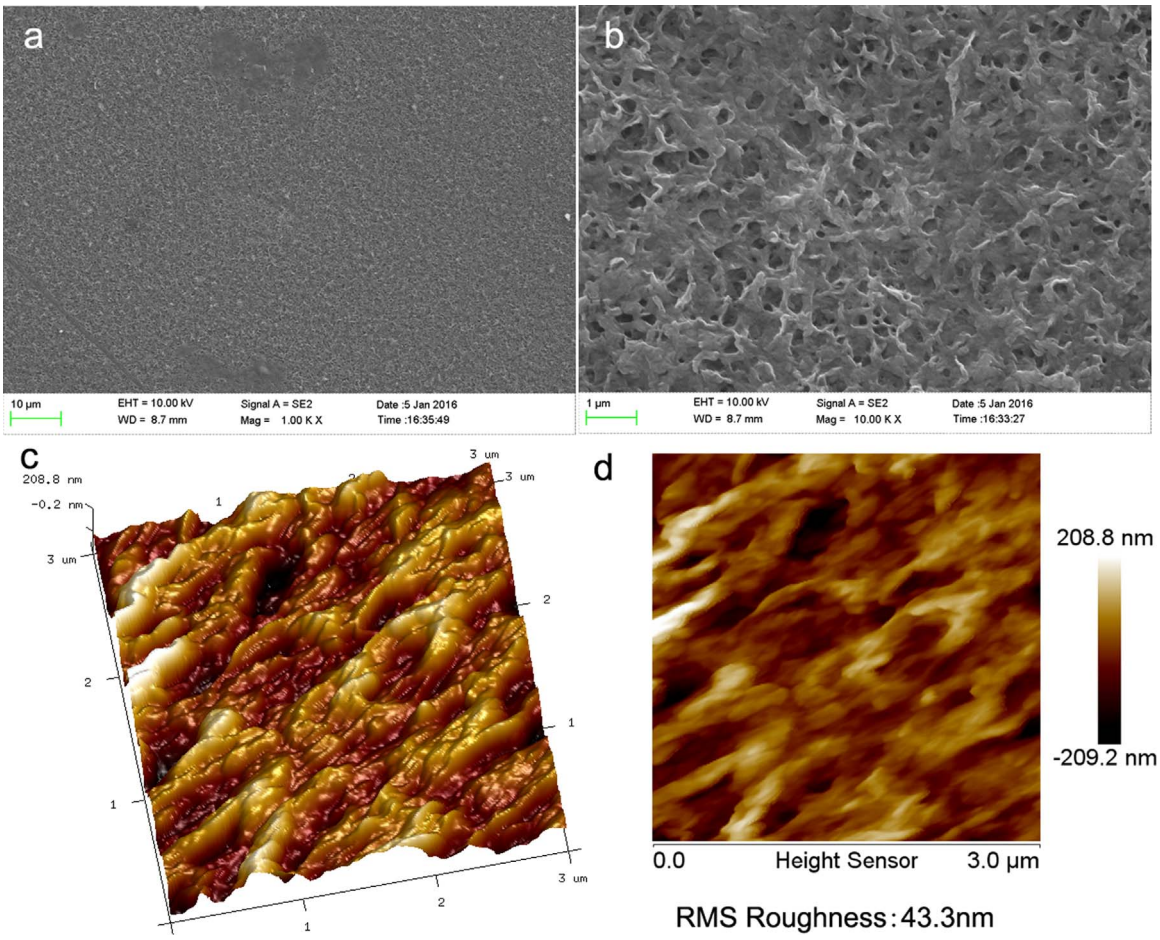

Fig. 1. (a) Surface morphologies of PANI film and (b) high magnification of the PANI film on FTO substrate. AFM images of the surface morphology of (c) 3D and (d) 2D height image with a 1 μm × 1 μm scale.

pressures. So far, relatively little research has been conducted on directly grown PANI on FTO substrate via a simple hydrothermal growth.

Herein, we report a hydrothermal approach that has been developed for synthesis of PANI film on FTO substrate directly by one-pot polymerization of aniline. Our study shows that the PANI are suitable for the build-up of thin films via hydrothermal method, and that the resulting films exhibit interesting electrochromic properties with high contrast and fast switching times.

2. Experiment

2.1. Materials

Aniline was purchased from Aladdin and distilled before use under reduced pressure. Ammonium persulfate($(NH_4)_2S_2O_8$, APS), anhydrous lithiumperchlorate ($LiClO_4$), propylene carbonate (PC),Dodecyl benzenesulfonic acid (DBSA) and Hexadecyltrimethyl ammonium bromide (CTAB) were of analytical grade and used without further purification. All the distilled water was used for sample preparation and characterization. The fluorinetin oxide (FTO) coated glass plates of thickness of 2.2 mm with resistance of 8–12 Ω sq^{-1} were purchased from NSG, Japan, and used as the substrate for PANI film.

2.2. Synthesis

PANI was directly grown on a fluorine-doped tin oxide (FTO) glass substrate using a hydrothermal method. The FTO substrates were cleaned with acetone, ethanol, finally rinsed with deionized water and dried in air. In a typical experimental procedure, 0.7288 g of CTAB was dissolved in 77 mL of H_2O with vigorous stirring to form a uniform solution. Then 0.2 mg of freshly distilled aniline was then added to CTAB solution. After that, 4 mL of DBSA was added to the solution and stirred for 10 min. To this mixture, a solution containing 0.2192 g of APS was slowly added into the monomer solution under vigorous stirring. After that, the entire solution was transferred into a Teflon vessel and the FTO substrate was placed at an angle against the wall of the autoclave with the conductive side facing down. The hydrothermal reaction was conducted at 160 °C for 3 h and then cooled overnight. After rinsed extensively with deionized water and dried in vacuum. The PANI film was uniformly coated on the FTO glass substrate.

2.3. Fabrication of the electrochromic device

The FTO coated with PANI thin film was fabricated as work electrode. The electrochromic devices with sandwiched structure of FTO/electrochromic layer/polymer gel electrolyte/FTO were fabricated according to the methods described in our previous publication [16]. The polymer gel electrolyte used was a mixture of 0.512 g of LiClO4, 2.8 g of PMMA, 8 g of propylene carbonate, and 28 g of acetonitrile.

2.4. Characterization

Scanning electron microscopy (SEM) images of PANI were recorded on a Zeiss Supra 55 field emission scanning electron microscope. Specimens for SEM experiments were made by placing a piece of FTO glass with PANI film on a conducting stage and were then observed with gold coating. The FTIR spectrum was acquired on a Perkin-Elmer