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A facile synthesis of polythiophene nanowires

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Abstract

Polythiophene nanowires have been synthesized by the gamma radiation-induced chemical oxidative polymerization method. The resultant fiber-like polymer structures were identified by the field-emission scanning electron microscopy with diameter of the order of 50–100 nm and a length of up to several millimeters. Different characterizations, e.g. elemental analysis, Fourier transform infrared, Raman spectroscopy, and X-ray photoelectron microscopy were utilized to prove that conducting polythiophene was synthesized successfully by this facile method.

Keywords: Conjugated polymers; Nanoparticles; Radiolysis polymerization; Facile synthesis

1. Introduction

Throughout the last few decades, electrically conjugated conducting polymers (CP) have rapidly become a subject of tremendous interest among academic and industrial researchers due to their curious electronic, magnetic, and optical properties [1–6]. Among the conjugated polymers, polythiophene (PTh) is one of the most studied polymers due to its flexibility, ease of doping, and good thermal and electrical stability that exhibit some unique advantages of PTh for the development of various applications [7–9]. PTh in both undoped and doped states have been studied for various applications, including organic field effect transitor, solar cells, sensors, electrochromic devices, and light emitting diodes [10–13]. The important factors in these considerations are environmental stability in the presence of oxygen or moisture and easy control of electrical and optical properties [7]. Heightened interest in one-dimensional electrical conductors and the need to produce nanoscale electrical connections has caused recent research to focus on conjugating polymer nanomaterials such as nanowires, nanotubes, nanobelts and nanocables [14–17].

In general, the "template synthesis" method, which involves using pores in a micro-porous membrane as a template for nanoscale fibers or wires formation, is an effective method for the synthesis of conjugating tubular polymers. Georger et al. initiated the template synthesis method; later, Martin et al. and other groups were able to apply the method successfully to the synthesis of various polymeric tubular forms [18–21]. Although the templating method has some advantages, it is cumbersome to remove the template from the final products. Wan et al. recently developed a simple method of in situ doping polymerization in the presence of β-naphthalene sulfonic acid as the dopant [22]. In situ doping polymerization is much easier without the nano/microporous membrane, as the template or the anchoring materials bind the polymer to the wall of the membrane, instead of the template synthesis method. More recently, gamma-irradiation has been used extensively to generate novel nano/microparticles of polymeric materials with unusual properties, since it can help prepare particles at room temperature and under ambient pressure. In addition, it is easily controlled and adaptable, and it cannot induce impurities into the materials [23–28]. Here, we show a facile synthesis route and the unique physical properties of a new constitutional view of the polythiophene nanowires, can be synthesized in a "templateless" fashion by the gamma radiation-induced chemical polymerization method. To the best of our knowledge, this is the first experimental evidence of the polythiophene

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nanowires synthesis route, via the use of radiolysis polymerization method.

2. Experimental detail

Thiophene monomer (99+%) was distilled under a reduced pressure and kept below 0 °C prior to use. Anhydrous iron (III) chloride ($FeCl_3$, oxidant), chloroform ($CHCl_3$), and other organic solvents were bought from Aldrich as reagent grade and used without further purification.

In a typical synthesis, anhydrous $FeCl_3$ (0.0125 M) in 100 ml of $CHCl_3$ solution was taken to a 250 ml capacity high-density polyethylene bottle and sonicated for 10 min at room temperature. Thiophene monomer (0.0063 M) with 50 ml of $CHCl_3$ solution was added quickly to the above solution. The resultant solution was deaerated by bubbling with argon to remove dissolved oxygen before irradiation. Then, it was sealed and radiated by a ^{60}Co γ-ray source at a rate of ca. 20 kGy for 1 h at room temperature under an ambient pressure. After irradiation, the sample was washed carefully with an excess of distilled water, methanol, hydrochloric acid (0.1 M), and acetone, respectively, to remove the unused initiator, and other impurities. The obtained black powder was dried under a vacuum dryer at room temperature for 24 h.

The instruments used in this work included an Elemental Analysis (EA) (CE Instruments model FISON EA-1110); a field-emission scanning electron microscope (FE-SEM) (Hitachi model S-4300); a Fourier transform infrared (FT-IR) (Bruker IFS 120HR); a laser Raman spectrometer equipped by Jobin-Yvon Horiba HR800 model (Coherent Innova 90C Fred^{TM} argon ion (Ar^+) as laser source); a Thermal Gravimetric Analysis (Dupont Model 9900/2100) in a nitrogen atmosphere, at a heating rate of 10 K/min in the temperature range of 0–800 °C; and an X-ray Photoelectron Spectroscopy (XPS) (VG Clam2 system).

3. Results and discussion

The typical morphology of PTh nanowires was characterized by using field-emission scanning electron microscopy (FE-SEM). As shown in Fig. 1, parts a and b show low-magnification of the FE-SEM images with a uniform view of the as grown lengthy unaligned and the as-grown aligned PTh nanowires array, respectively. A high-magnification close-up view of the individual PTh nanowires shows that a single nanowire has an average diameter in the range between 50 nm and 100 nm and the length of the wire can be up to several millimeters (Fig. 1c). These structures were found from the parent solutions with typical concentrations of 0.0063 M thiophene and 0.0125 M anhydrous ferric chloride in chloroform solutions as described in details in the experimental section. To observe the effects of monomer and oxidant concentrations, we used different concentrations of monomer and oxidant as shown in Fig. 2. In this case, we found the highest yield of polythiophene nanowires in the concentrations of 0.0063 M thiophene and 0.0125 M anhydrous ferric chloride in chloroform solutions (Fig. 2a). In upcoming discussion, we will only show the explanation of this sample.

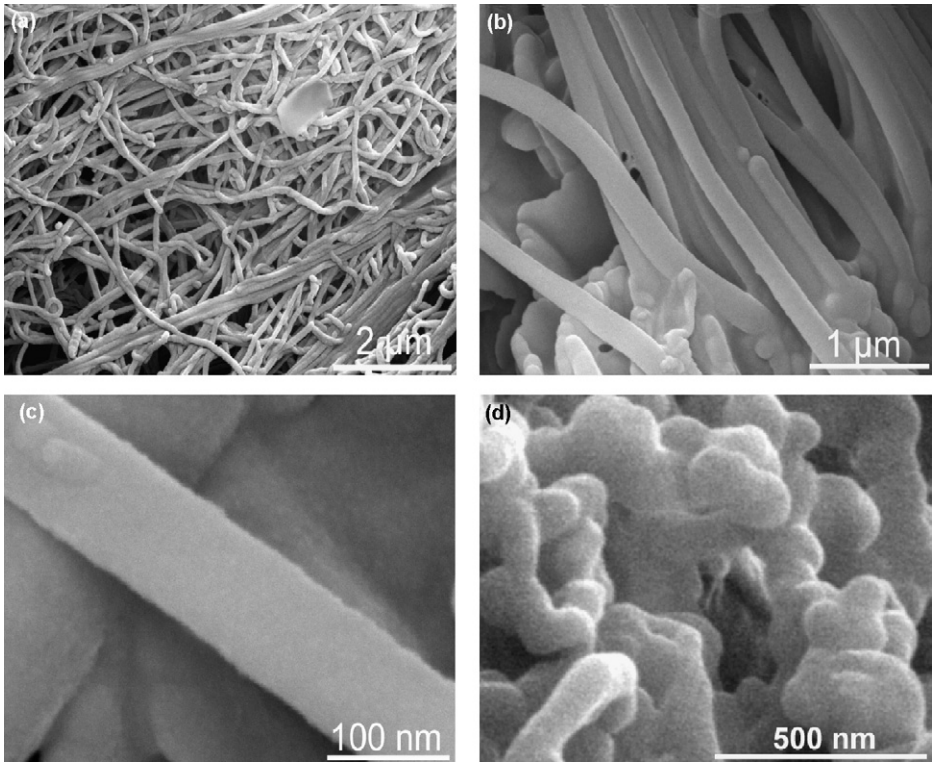

Fig. 1. FE-SEM images of the as-grown polythiophene nanowires: (a) the lengthy unaligned nanowires (scale bar: 2 μm), (b) the aligned nanowires array (scale bar: 1 μm), (c) a close-up view of a single nanowire (scale bar: 0.2 μm) produced by the radiolysis polymerization method, and (d) polythiophene aggregation produced by the ordinary chemical oxidative polymerization method (scale bar: 0.5 μm).