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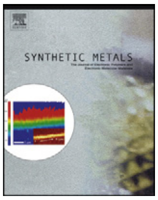

# Facile synthesis of high-quality ultralong poly(aniline-*co*-*p*-phenylenediamine) nanofibers

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ABSTRACT

High-quality ultralong poly(aniline-*co*-*p*-phenylenediamine) nanofibers have been synthesized successfully by one-step chemical copolymerization of aniline and *p*-phenylenediamine using ammonium peroxydisulfate as the oxidant in aqueous solution. The addition of *p*-phenylenediamine in conventional polymerization system plays an important role in changing the bulk morphologies of polyaniline from irregular particle agglomerates to nanofibers. This process is rapid, facile, and free of any template and surfactant. The influences of synthetic parameters, such as the molar ratios of aniline and *p*-phenylenediamine, the molar ratios of monomer and ammonium peroxydisulfate, and the concentrations of HCl, on the morphologies and molecular structures of the resulting products have been investigated for elucidating the formation mechanism of poly(aniline-*co*-*p*-phenylenediamine) nanofibers.

## 1. Introduction

During the past few decades, conducting polymers, such as polypyrrole, polyaniline, polythiophene, and polyacetylene, have received great attention due to their fascinating electrical, optical, and electrochemical properties derived from the conjugated $\pi$-electron system. Unlike many other conducting polymers, polyaniline is unique in view of its easy synthesis, remarkable environmental stability, and reversible acid–base doping–dedoping process [1–4]. However, the conventional chemical oxidative polymerization of aniline in dilute aqueous acids using ammonium peroxydisulfate (APS) oxidant yields irregular granular aggregates and a small fraction of nanofibers.

In recent years, one-dimensional (1D) polyaniline nanostructures have aroused increasing interests with the dual advantages of both low-dimensional system and organic conductors, and have potential applications in chemical sensors [5], polymeric conducting molecular wires [6], actuators [7], and biosensors [8–10]. Several different routes have been developed to synthesize 1D polyaniline nanostructures with or without the aid of templates. As reported previously, polyaniline nanofibers appear to be the intrinsic morphology of polyaniline even in conventional synthesis of polyaniline, and it seems unnecessary for the hard or soft templates to form the 1D polyaniline nanostructures [11–13]. In the past few years, other "templateless" techniques including interfacial polymerization [13], dilute polymerization [14,15], rapid mixing reactions [16], oligomer initiated polymerization [17], and falling pH polymerization [18–20] have been developed to produce polyaniline nanofibers. In oligomer initiated polymerization for synthesis of polyaniline [17], the introduction of a small amount of aniline dimer and other structurally related additives can accelerate the rate of polymerization of aniline, which changes the bulk morphology of polyaniline from irregular particle agglomerates to nanofibers.

Recently, polyaniline derivatives, which bear various functional groups, exhibit some unique properties and have also been extensively investigated [21]. Among them, poly(phenylenediamine) homopolymer exhibits high thermostability, which is reported to be a highly aromatic polymer containing 2,3-diaminophenazine or quinoraline repeating unit [22]. Three isomers of *o*-, *m*-, and *p*-phenylenediamines have became important subject of active investigation since they have performed better reversible redox reactivity, complexability, electroactivity, gas permselectivity, and electrochromism. The good properties make them have promising applications, such as electrocatalyst, corrosion protection, sensors, detectors, and heavy metal ion sorbent [23–27]. Herein, we report the facile and rapid synthesis of high-quality ultralong poly(aniline-*co*-*p*-phenylenediamine) [poly(ANI-*co*-p-PDA)] nanofibers by one-step chemical copolymerization of aniline

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and p-phenylenediamine using APS as the oxidant in aqueous solution.

## 2. Experimental

### 2.1. Synthesis of poly(ANI-co-p-PDA) nanofibers

All reagents used in our experiment are of analytical purity and used without further purification. In a typical synthesis, aniline (2.25 mmol) and p-phenylenediamine (p-PDA, 0.75 mmol) were dissolved in 30 mL of 1 M HCl aqueous solution with magnetic stirring to form a transparent aqueous solution and then cooled to 0–5 °C. The polymerization reaction was initiated by steadily adding the pre-cooled solution containing 1.5 mmol of APS in 20 mL of 1 M HCl aqueous solution to the monomer solution, which is under violent stirring. Upon the addition of APS, a rapid color change is observed with the naked eye. The polymerization reaction was carried out for 20 h at 0–5 °C without any disturbance. The dark green product was isolated from the dispersion by centrifugation, washed with deionized water and ethanol several times, and dried at 80 °C for 24 h. In all reactions, the total concentration of aniline and p-PDA is kept constant. Herein, the pure polyaniline and poly(p-PDA) was synthesized chemically via the similar procedure above.

### 2.2. Characterization

The morphologies and sizes of poly(ANI-*co*-*p*-PDA) were characterized by field-emission scanning electron microscopy (FE-SEM, JSM 6700F) and transmission electron microscopy (TEM, JEM 2000EX). The molecular structures of poly(ANI-*co*-*p*-PDA) sample were measured by Fourier transform infrared (FTIR, Nicolet Magna IR-750 spectrophotometer) spectroscopy using a dried poly(ANI-*co*-*p*-PDA) powder and UV–vis spectroscopy (Cary 500 UV–vis–NIR spectrophotometer) using poly(ANI-*co*-*p*-PDA) dispersions in deionized water.

## 3. Results and discussion

Fig. 1 shows typical SEM and TEM images of pure polyaniline and poly (ANI-*co*-*p*-PDA) (the molar ratio of aniline and *p*-PDA = 3:1) nanostructures under the same polymerization condition. As shown in Fig. 1A, pure polyaniline sample is composed of a large quantity of interconnected nanofibers and a small fraction of nanoparticle aggregates. The diameters and length of polyaniline nanofibers are in the range of 30–50 nm and 0.5–1 μm, respectively. However, low-magnification SEM image in Fig. 1B reveals that poly (ANI-*co*-*p*-PDA) sample exhibits nanofibrillar morphologies with length up to several tens of micrometers. High-magnification SEM image in Fig. 1C reveals that poly (ANI-*co*-*p*-PDA) nanofibers with smooth surfaces have diameters in the range of 25–65 nm, which can be further demonstrated by TEM observation (Fig. 1D). In comparison with that in Fig. 1A, poly (ANI-*co*-*p*-PDA) nanofibers are less entangled and interconnected, which demonstrates that *p*-PDA can leads to a change in morphology from an entangled nanofiber mat of pure polyaniline to longer and less entangled nanofibers.

The influences of synthetic parameters, such as the molar ratios of aniline and *p*-PDA, the molar ratios of monomer and APS, and the concentrations of HCl, on the morphologies and molecular structures of the resulting products have been investigated. Among them, the molar ratios of aniline and *p*-PDA are crucial for the formation of poly(ANI-*co*-*p*-PDA) nanofibers. Fig. 2 represents SEM images of poly(ANI-*co*-*p*-PDA) nanostructures synthesized with different molar ratios of aniline and *p*-PDA in 0.1 M HCl solution. As the molar ratio of aniline and *p*-PDA is too high (e.g., 40:1), the nanofibers are more entangled and coarser than that in Fig. 1B. It is clear that some nanoparticles grow on the surfaces of polyaniline nanofibers, indicating that the amount of *p*-PDA is not enough to suppress the heterogeneous nucleation on the surfaces of polyaniline nanofibers. As the molar ratio of aniline and *p*-PDA is increased to 1:1, the similar phenomenon to that of Fig. 1B is observed. However, as the molar ratio of aniline and *p*-PDA is increased further (e.g., 1:3), the diameters of the nanofibers are increased to 40–90 nm, and the nanofiber surfaces become coarser. When the

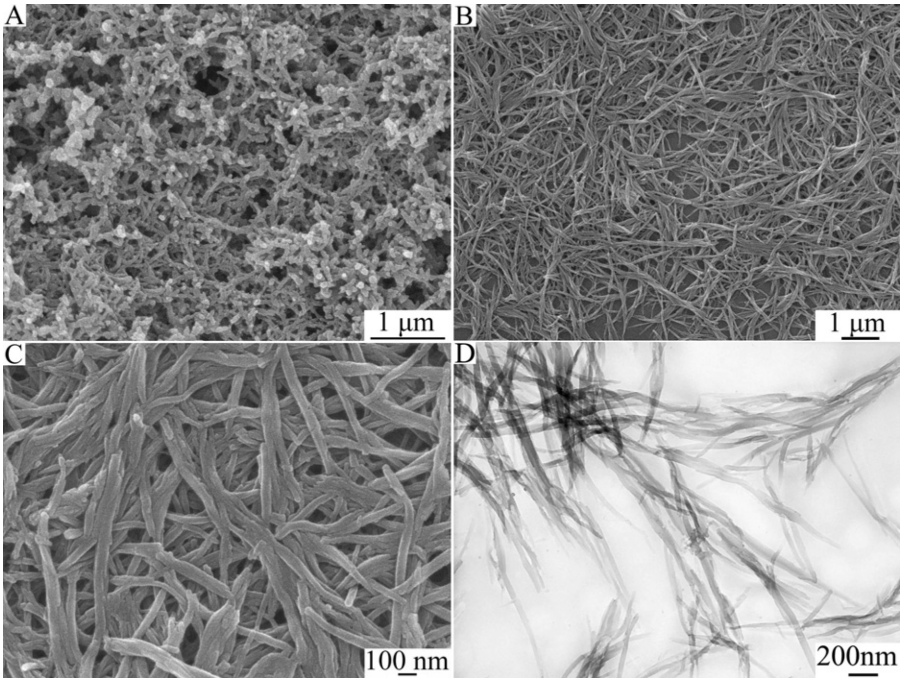

**Fig. 1.** SEM (A) image of polyaniline nanofibers without *p*-PDA. SEM (B and C) and TEM (C) images of poly(ANI-*co*-*p*-PDA). ([aniline]/[*p*-PDA] = 3:1, [aniline + *p*-PDA]/[APS] = 2:1, [HCl] = 0.1 M.)