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Synthesis of radially aligned polyaniline dendrites

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Abstract

Radially aligned polyaniline dendrites with nanotube junctions have been synthesized using tartaric acid as the dopant without the aid of any surfactants. These dendritic nanotubes with 80–400 nm in outer diameter, 30–50 nm in wall thickness, and several micrometers in length can self assemble into urchin-like nanostructures. The geometrical shape of the individual branch is a cone. The nanotube junctions may provide potential applications in nanoelectronic devices. Furthermore, the influences of other organic acid, such as citric acid, oxalic acid, and acrylic acid, on the morphologies on polyaniline nanostructures have been investigated.

Keywords: Dendrite; Nanostructures; Polyaniline

1. Introduction

Much attention has been paid to the study of one-dimensional (1D) nanostructures of conjugated polymers because of their novel physical properties. Controlled alignment is more critical for potential applications such as in polymeric conducting molecular wires [1], chemical sensors [2–5], biosensors [6], light-emitting and microelectronic devices [7–9]. Among the family of conjugated polymers, polyaniline is unique due to its simple and reversible acid–base doping–dedoping chemistry. In the past few years, great efforts have devoted to the fabrication of aligned conjugated polymers nanotubes or nanofibers by chemical or electrochemical oxidative polymerization of the corresponding monomer with the aid of templates or structural directing molecules. Zeolite channels [1], track-etched polycarbonate [10], and anodized alumina [11] were reported to be capable of directing the growth of aligned polyaniline nanotubes or nanofibers. However, the polymeric structures with preferred orientation could be destroyed easily when released from the template. Feng et al. [12] deposited a thin polyaniline coating on the surface of aligned multiwalled carbon nanotubes. Recently, Grady et al. [13] fabricated nanostructures of polyaniline and polypyrrole with controlled morphologies on atomically flat surfaces using adsorbed surfactant as structural directing molecules. Liang et al. [7] designed a three-step electrochemical deposition procedure to synthesize large arrays of uniform and oriented polyaniline nanowires. Wan et al. [14,15] reported a route to synthesize submicrometer-sized tube junctions and dendrites of polyaniline in the presence of different dopants. Our group [16] synthesized dendritic polyaniline nanofibers in a cationic surfactant gel. The development of simple, mild, and effective methods for creating novel assemblies of 1D nanostructures of conjugated polymer is of importance to nanotechnology and remains a key research challenge. In this paper, we report a facile and surfactantless approach to synthesize the radially aligned polyaniline dendrites with rectangular hollow interiors and nanotube junctions.

2. Experimental part

2.1. Synthesis of radially aligned polyaniline dendrites

An optimized procedure for the synthesis of radially aligned polyaniline dendrites is described as follows: 0.37 g of D,L-tartaric acid (used as the dopant) and 0.23 g of aniline were dissolved in 40 mL of deionized water. Ammonium peroxydisulfate (0.28 g, used as the oxidant) was dissolved in 20 mL of deionized water. The aqueous solution of ammonium peroxydisulfate was added to the solution of tartaric acid and

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aniline in one portion, and then the resulting solution was stirred for 1 min at 0 °C. The polymerization reaction was carried out under static conditions for 36 h at 0 °C. The resulting polyaniline precipitate was filtered, washed with deionized water several times, and dried at room temperature for 24 h. In all reactions, the concentrations of organic acid, such as tartaric acid, citric acid, oxalic acid, and acrylic acid, are 0.04, 0.04, 0.06 and 0.12 M, respectively.

2.2. Characterization

The morphologies of polyaniline nanostructures were characterized by field emission-scanning electron microscopy (FE-SEM, JSM 6700F) and transmission electron microscopy (TEM, JEM 2000EX). The molecular structures of the as-synthesized radially aligned dendritic polyaniline nanostructures were measured by Fourier transform infrared (FTIR) spectroscopy and UV–vis spectroscopy. FTIR spectrum was determined on a Nicolet Magna IR-750 spectrophotometer using KBr pressed disk. UV–vis spectrum was measured on a Cary 500 UV–vis–NIR spectrophotometer (the products were dispersed in deionized water).

3. Results and discussion

Fig. 1 shows typical SEM and TEM images of the as-synthesized polyaniline nanostructures (the concentration of tartaric acid = 0.04 M). Interestingly, the assembly of polyaniline in Fig. 1(A) is highly reminiscent of a sea urchin with size up to 20–25 μm, which is different from that of Wan's group reported. The urchin-like polyaniline nanostructures are composed of radially aligned uniform nanofibers (Fig. 1(B))

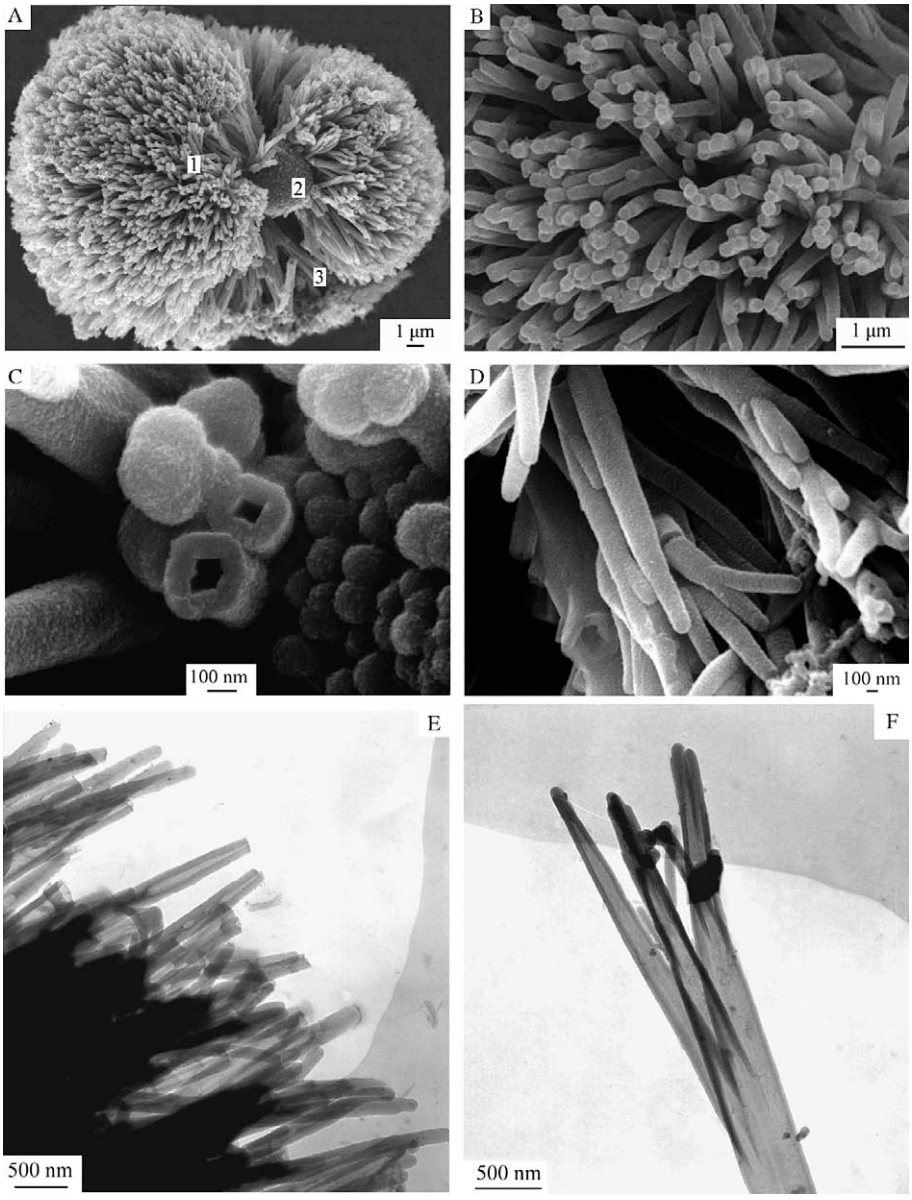

Fig. 1. SEM and TEM images of the as-synthesized radially aligned polyaniline nanotubes. (A) Low magnified SEM image; (B), (C), and (D) show magnified SEM images of boxes 1, 2, and 3 in (A), respectively; (E) TEM image of the edge of polyaniline nanostructures; (F) TEM image of a representative polyaniline dendrite.

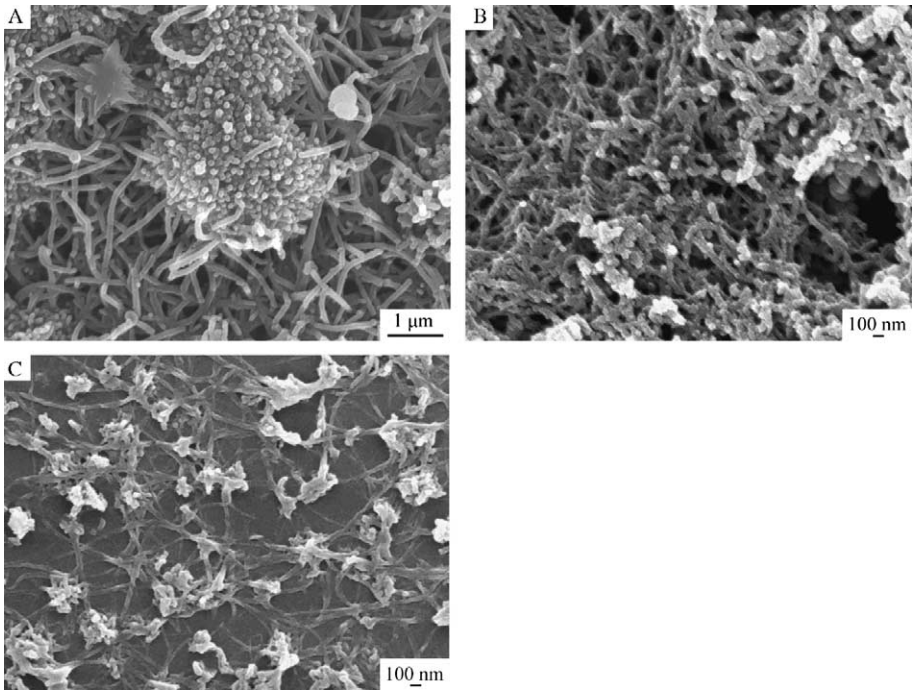

Fig. 2. SEM images of polyaniline nanostructres synthesized with different dopants. (A) Citric acid; (B) oxalic acid; (C) acrylic acid.

and a core (Fig. 1(C)). The core seems to comprise vestigial nanorods and nanoparticles. Some fractured nanofibers have rectangular hollow interiors in cross section, indicating that these oriented nanofibers are nanotubes. As far as the rectangular hollow interiors are concerned, these tubes are different from the previously reported nanotubes [14]. In a magnified SEM image (Fig. 1(D)), these nanotubes are often linked together to form Y-junctions and then assemble into polyaniline dendrites. It is clear that the geometrical shape of the individual branch is a cone with length of several micrometers. The outer diameters decrease from 400 to 80 nm along the lengths of the cone. Fig. 1(E) represents a TEM image of the edge in the as-synthesized radially aligned dendritic polyaniline nanostructures. It reveals that the cones have tubular structures with wall thickness of 30–50 nm. The outer diameters and lengths of the branches are consistent with SEM images. A representative TEM image of polyaniline dendrite is shown in Fig. 1(F). It seems that several tube branches with a close end can grow from the same trunk to form the complicated junctions, which is reminiscent of the vessels in the bodies of animals and plants.

The effects of the dopants on the morphologies of polyaniline are investigated. Fig. 2(A) shows a SEM image of polyaniline nanostructures synthesized with citric acid as dopant. It is found that polyaniline nanofibers grown from the particle aggregates are unoriented. The diameters and lengths of polyaniline nanofibers are in the range of 80–90 nm and several micrometers, respectively. However, when oxalic acid is used instead of tartaric acid or citric acid, only polyaniline nanofibers (Fig. 2(B)) having diameters 40–60 nm are obtained, which are similar to that of Kaner's group reported [17]. Polyaniline nanostructures synthesized with acrylic acid as dopant (Fig. 2(C)) are also composed of nanoparticulate aggregates and nanofibers with diameters of 40–60 nm.

Fig. 3 presents FTIR spectrum of the as-synthesized radially aligned dendritic polyaniline nanostructures. The peaks at 1574 and 1505 cm^{-1} are assigned to the C=C stretching of quinoid rings and benzenoid rings, respectively. The peak at 1302 cm^{-1} corresponds to stretching of C–N. The peaks at 1146 and 823 cm^{-1} are attributed to the aromatic C–H in-plane bending and the out-of-plane deformation of C–H in the 1,4-disubstituted benzene ring, respectively [14–16,18–20]. A typical UV–vis spectrum of the as-synthesized radially aligned dendritic polyaniline nanostructures is shown in Fig. 4. The peaks at 355, 440 and 870 nm are attributed to $\pi \rightarrow \pi^*$ transition, polaron band $\rightarrow \pi^*$ transition, and the π to the localized polaron band of doped polyaniline in its emeraldine salt form, respectively [21]. FTIR and UV–vis results show that

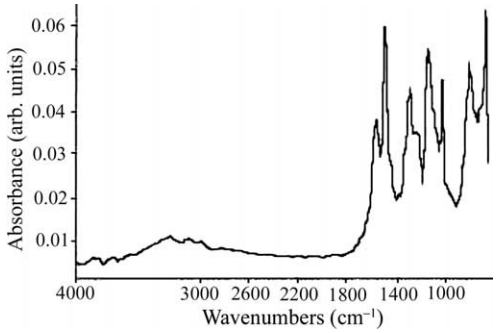

Fig. 3. FTIR spectrum of the as-synthesized radially aligned polyaniline nanotubes.

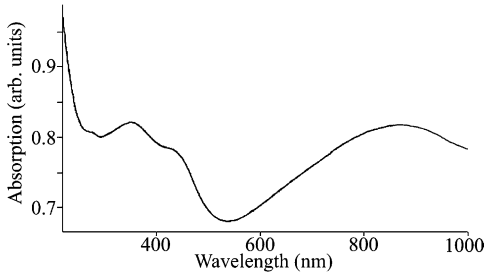

Fig. 4. UV–vis spectrum of the as-synthesized radially aligned polyaniline nanotubes.

the state of the as-synthesized radially aligned nanotubes is doped polyaniline in its emeraldine salt form.

The synthetic process is very simple, mild, and free of any surfactants. The formation of radially aligned dendritic polyaniline nanotubes with rectangular hollow interiors is probably related to the molecular structures of the organic dopants, the linear nature of polyaniline chains and the polymerization reaction rate [22]. Tartaric acid has hydrophobic alkyl chain and hydrophilic –COOH. Before polymerization, aniline and tartaric acid can react with each other to form a soluble salt at 0 °C. The early stage of oxidative polymerization is slow [23], because the reaction pH is higher than that of Kaner's synthesis route [17], so the formed polyaniline oligomers and tartaric acid can have enough time to assemble into micelles, which can aggregate together through the hydrogen-bonding interactions. Polymerization can proceed on these aggregates to form polyaniline cores (Fig. 1(C)). The rigid molecular chain of polyaniline can induce the micelles to be elongated, resulting into the formation of polyaniline nanotubes [14]. The polymerization growth on the surface of the core may result in the radially alignment of polyaniline nanotubes. The formation of these rectangular hollow interiors in polyaniline nanotubes may be ascribed to the pressure among the close packed nanotubes based on the core. The hydrogen bonding interactions between the dopants, such as citric acid, oxalic acid, and acrylic acid, and polyaniline molecules may be different from that of tartaric acid due to their different molecular structures, so the morphologies of polyaniline are affected. The formation mechanism of the radially aligned dendritic polyaniline nanotubes with rectangular hollow interiors needs further investigation.

4. Conclusion

In summary, we have demonstrated a facile and surfactantless route to the synthesis of radially aligned polyaniline dendrites with rectangular hollow interiors using tartaric acid as the dopant. These dendritic nanotubes with 80–400 nm in outer diameter, 30–50 nm in wall thickness, and several micrometers in length can self assemble into urchin-like nanostructures. The geometrical shape of the individual branch is a cone. The nanotube junctions may provide potential applications in nanoelectronic devices.

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