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Novel interfacial polymerization for radially oriented polyaniline nanofibers

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Abstract

A novel interfacial polymerization method derived from the self-assembly method is presented in this paper for the generation of radially oriented polyaniline nanofibers. Salicylic acid (SA) was used as dopant and the diameters of polyaniline-SA nanofibers range from 300 to 500 nm. Compared with the previous interfacial polymerization methods, no organic solution was added in our method. The organic phase formed in our experiment is made up of a monomer (aniline) and a dopant (salicylic acid: SA) and their amounts were increased. Scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectra are used to characterize the products.

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Keywords: Interfacial polymerization; Polyaniline; Nanofibers; Salicylic acid

1. Introduction

Oriented one-dimensional (1D) nanostructures have attracted much attention. Especially, oriented 1D conducting nanostructures gain special attention for their various applications ranging from chemical and biological sensing and diagnosis to energy conversion and storage (photovoltaic cells, batteries and capacitors, and hydrogen-storage devices), light-emitting display devices, catalysis, drug delivery, separation, microelectronics, and optical storage [1–3]. A variety of synthetic methods, including electrochemical deposition [4], templates [5,6], self-assembly [7–9], electrospinning [10–12], interfacial polymerization [13–15], seeding growth [16,17], and oligomer-assisted polymerization [18], have been developed for preparing 1D conducting polymer nanostructures. But, to the best of our knowledge, oriented 1D conducting polymer nanostructures were mostly obtained through the template method [5,6], in which the formation of arrays of oriented polymer nanorods or tubes involves carefully etching away the membrane without disturbing the conducting polymer nanostructures. Etching away the template-supports often caused the polymer to collapse into structures without preferred orientation

[19]. Recently Liang et al. reported the fabrication of large arrays of conducting polymer nanowires through electrochemical deposition [4] but this method needs special conditions (conducting microelectrode surface or reduced current density). So it is foreseen that finding a novel and simple synthetic method for the preparation of oriented conducting polymer nanofibers is essential to modern science.

Herein, we report a facile synthetic method for large arrays of radially oriented polyaniline nanofibers via a novel interfacial polymerization. Compared with the previous methods, it is easier to prepare oriented conducting polymer nanostructures on flat surfaces, therefore opening up new opportunities for designing devices.

2. Experimental section

2.1. Materials

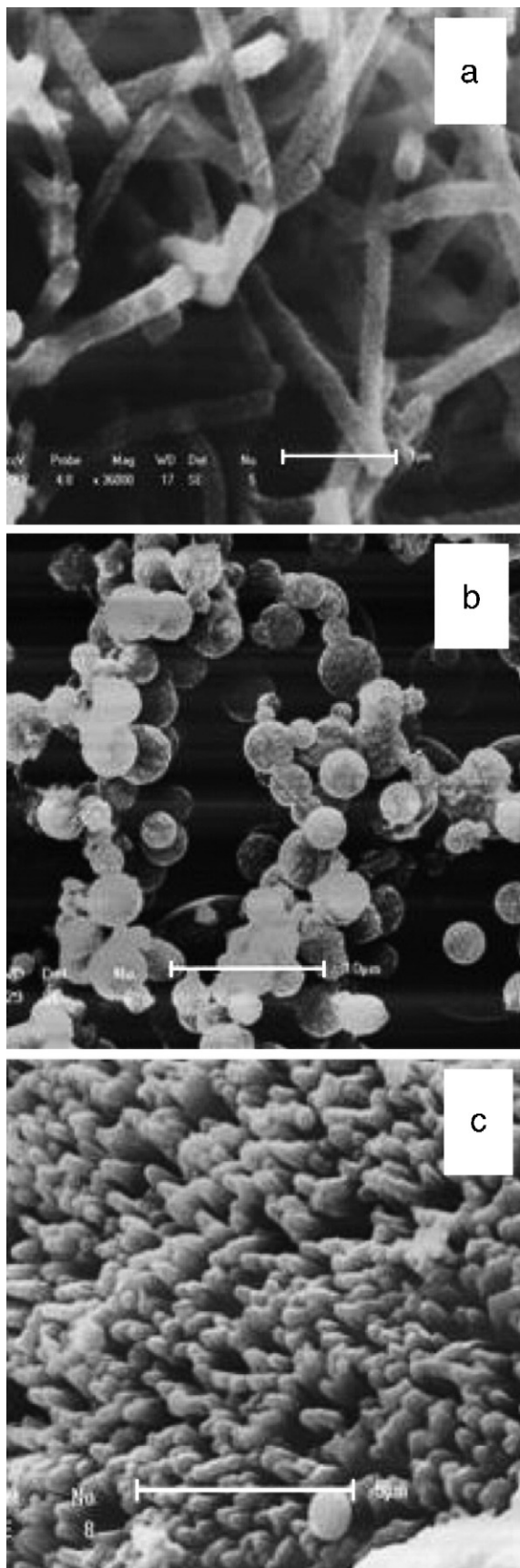
Aniline was supplied by Beijing Chem. Co (China) and distilled under reduced pressure before the experiment; salicylic acid was purchased from Nankai Chem. Co.

2.2. Preparation of radially oriented polyaniline-SA nanofibers

In a typical synthesis of well-aligned polyaniline-SA nanofibers, *in-situ* doping polymerization started in the presence

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of salicylic acid as dopant. 4×10^{-3} mol aniline (Beijing Chem. Co., distilled under reduced pressure) and 4×10^{-3} mol salicylic acid (SA: Nankai Chem. Co.) were dissolved in 20 mL of deionized water by ultrasonic stirring at 35 °C for 1 h. Then, the solution was cooled down to room temperature rapidly and poured into a culture dish. A piece of glass was immersed in the solution vertically. 0.5 h later, 20 mL of the ammonium peroxide sulfate (APS, 0.4 M) solution was then added. The reaction was left for 15 h at room temperature. Finally, the polyaniline-SA precipitates on the glass were washed with deionized water for four times, and dried at room temperature.

2.3. Characterization

Scanning electron microscopy (SEM) images of these samples were recorded on a SHIMADZU SSX-550, Japan. Fourier transform infrared (FTIR) spectra of these samples were recorded on a BRUKER VECTOR 22.

3. Results and discussion

Wan et al. have reported the self-assembly method for polyaniline precipitates (nanofibers and nanospheres) by controlling the concentration ratio of dopant and monomer (aniline) [7–9]. In our experiment, the concentration ratio of dopant [salicylic acid: SA] and aniline is higher than those reported by Wan. Scanning electron microscopy (SEM) is used to track the obvious changes of polyaniline-SA precipitates with an increasing concentration ratio of SA and aniline (the concentration of aniline is 0.2 M). When the concentration ratio of [SA]/[aniline] is 1:10, entangled polyaniline-SA nanofibers (a.v. 220 nm) are the main products (Fig. 1a); as the concentration ratio of [SA]/[An] is 5:10, polyaniline-SA hollow microspheres (Fig. 1b) take the place of nanofibers, which is consistent with the previous report [9]. However, when the concentration ratio of [SA] to [An] is 9:10, the extraordinary change emerged, the radially oriented polyaniline-SA nanofibers (Fig. 1c) could be obtained. The diameters of the oriented polyaniline nanofibers ranged from 300 to 500 nm.

To better know the formation conditions of the radially oriented polyaniline-SA nanofibers, a series of experiments have been done as shown below (keeping the concentration ratio of [SA]/[aniline]/[APS] at 1:1:1). When the concentration of aniline is 0.1 M, polyaniline precipitates were mainly made up of sparse and a little twisted nanofibers with the diameter ranging from 300 nm (Fig. 2a). As the concentration of aniline was enhanced to 0.15 M, compact and oriented polyaniline-SA nanofibers with the average diameter of 400 nm (Fig. 2b) can be detected. Till the concentration of aniline reached 0.225 M, the morphologies of oriented polyaniline-SA nanofibers (Fig. 2c and d) changed a little, the diameter increased from 450 nm (0.20 M) to 500 nm (0.225 M). From this SEM image, it can be clearly seen that the diameters of these polyaniline precipitates became thicker by increasing the concentration of aniline.

As illustrated by Huang [13,14] that in an immiscible organic (mixture of aniline and organic solvent)/aqueous (acid and APS solution) biphasic system, polyaniline nanofibers were obtained in the aqueous phase after the interfacial polymerization, that is to say polyaniline nanofibers grow from the organic phase to aqueous phase during the interfacial

Fig. 1. SEM images of the different polyaniline-SA precipitates of the obvious changes of polyaniline-SA precipitates by varying the concentration ratio of [SA] to [aniline]. The concentration ratio of [SA] to [aniline] is 1:10 (a), 5:10 (b), and 9:10 (c), respectively. The concentration of aniline is 0.2 M.

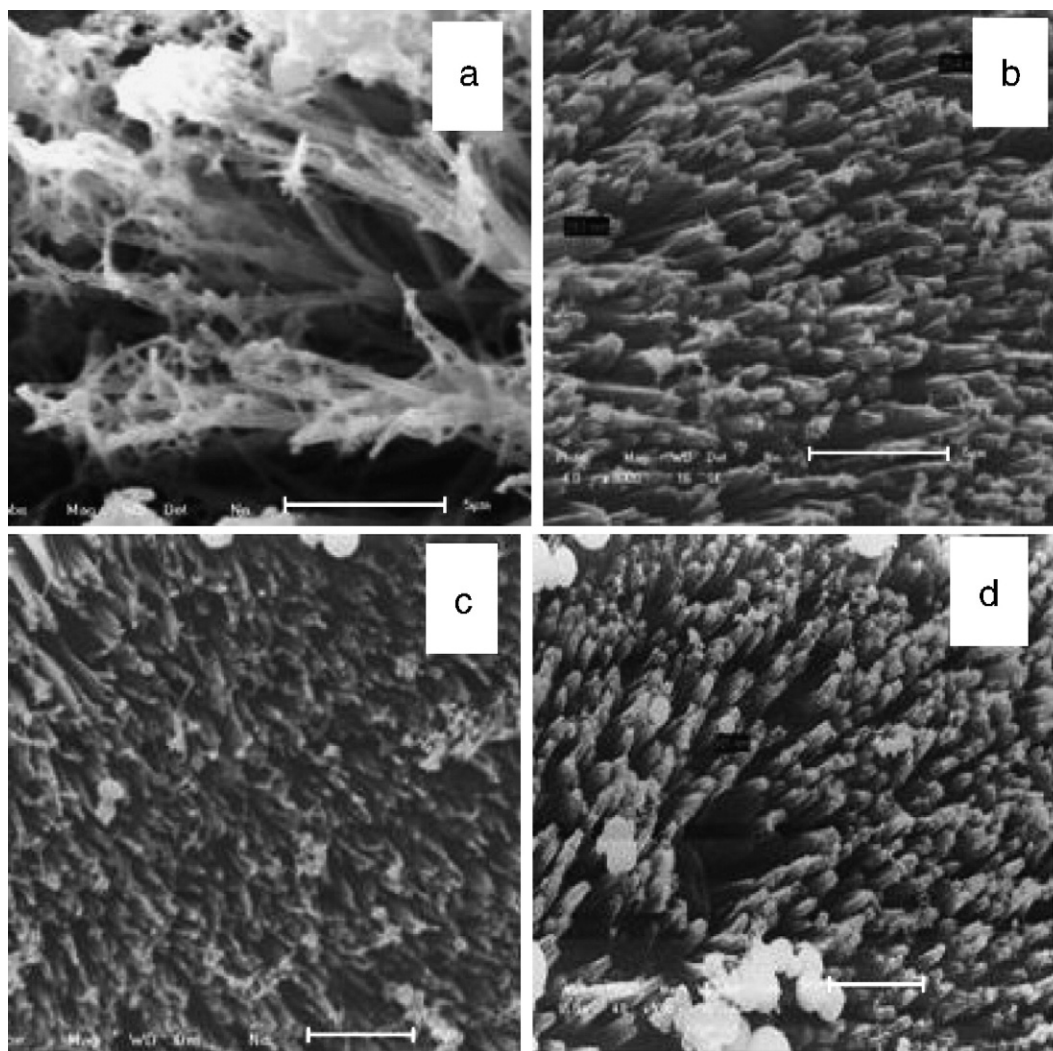


Fig. 2. SEM images of the changes of polyaniline-SA nanofibers by varying the concentration of aniline. The concentration of aniline is 0.10 M (a), 0.15 M (b), 0.20 M (c), and 0.225 M (d), respectively. The concentration ratio of [SA]/[aniline]/[APS] is kept at 1:1:1.

polymerization. This formation mechanism can be also applied in our experiment. For the high concentration of SA and aniline (keeping the concentration ratio of [SA]/[aniline]/[APS] at 1:1:1, the concentration of aniline is 0.15 M), some elliptical organic phase consisting of aniline doped with SA can form inside the distilled water in our experiment. When the APS solution was added, these elliptical organic-cores were surrounded by the aqueous phase containing oxidant (APS), resulting in big elliptical polyaniline-SA precipitates which existed among the products (Fig. 3a). Just from this time polymerization began, in which polyaniline-SA nanofibers grew from the elliptical organic-cores to aqueous phase. For the steric hindrance, all the fibers grew radially oriented and parallel to each other (Fig. 3c and d). Fig. 3d shows the SEM image of polyaniline precipitates' cross-section part, indicating that these polyaniline precipitates have lengths of 15–20 μm .

Fig. 4 shows the Fourier transform infrared (FTIR) spectrum of the as-prepared radially oriented polyaniline-SA nanofibers obtained in our experiment. In the FTIR, the characteristic peaks at 1567 and 1483 cm^{-1} can be assigned to the stretching vibration of the quinoid ring and benzenoid ring, respectively. The band observed at 1300 cm^{-1} corresponds to C–N stretch vibration of secondary aromatic amine. These characteristic vibration peaks were identical to those of pure polyaniline prepared using the common method [20].

4. Conclusion

In conclusion, radially oriented polyaniline-SA nanofibers were successfully synthesized using a simple and direct interfacial polymerization without templates, microelectrode, or special devices. In contrast to the previous methods, our method is simpler and more effective. Additionally, we believe that these radially oriented polyaniline-SA nanostructures will have a great potential for microsensors and other microelectronic and optical devices. Most importantly, the phenomenon of interfacial polymerization derived from the self-assembly method has been observed, for the first time, by simply changing the concentration ratio of monomer [aniline] and dopant [SA], which can provide a novel route to design and synthesize the conducting polymer nanostructures.

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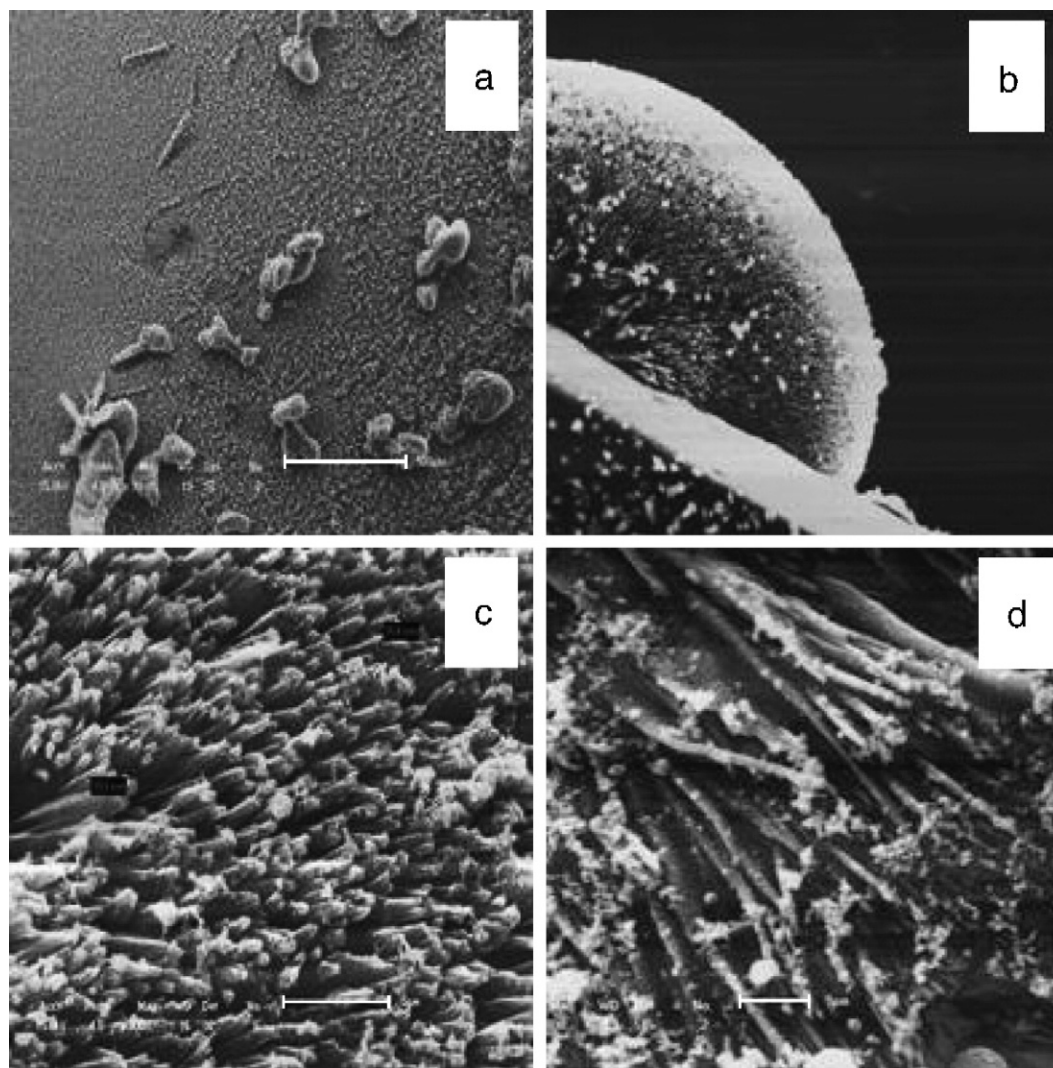


Fig. 3. SEM images of the elliptical precipitates made up of oriented polyaniline-SA nanofibers. The magnifications of (a), (b), and (c) are $\times 90$, $\times 800$, and $\times 8000$, respectively. (d) Cross-section part of polyaniline-SA nanofibers. The concentration ratio of [SA]/[aniline]/[APS] is kept at 1:1:1 and the concentration of aniline is 0.15 M.

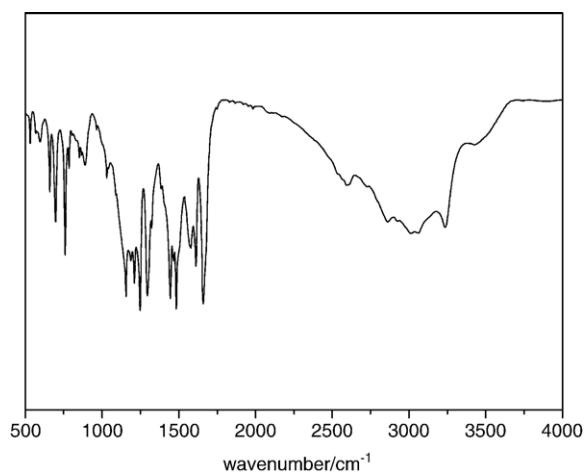


Fig. 4. FTIR spectrum of the as-prepared oriented polyaniline-SA precipitates.

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References

- [1] A.G. MacDiarmid, *Rev. Mod. Phys.* 73 (2004) 701.
- [2] K. Doblhofer, K. Rajeshwar, *Handbook of Conducting Polymers*, Marcel Dekker, New York, 1998 Chap. 20.
- [3] D. Kumar, R.C. Sharma, *Eur. Polym. J.* 34 (1998) 1053.
- [4] L. Liang, J. Liu, G.J. Exarhos, Y. Lin, *Angew. Chem., Int. Ed. Engl.* 41 (2002) 3665.
- [5] C.R. Martin, *Science* 266 (1994) 1961.
- [6] C.R. Martin, *Acc. Chem. Res.* 28 (1995) 61.
- [7] L. Zhang, M. Wan, *Nanotechnology* 13 (2002) 750.
- [8] Z. Wei, Z. Zhang, M. Wan, *Langmuir* 18 (2002) 917.
- [9] G. Li, Z. Zhang, *Macromolecules* 37 (2004) 2683.
- [10] D.H. Reneker, I. Chun, *Nanotechnology* 7 (1996) 216.

- [11] I.D. Norris, M.M. Shaker, F.K. Ko, A.G. MacDiarmid, *Synth. Met.* 114 (2000) 109.
- [12] N.J. Pinto, P. Carrión, J.X. Quiñones, *Mater. Sci. Eng., A Struct. Mater.: Prop. Microstruct. Process.* 366 (2004) 1.
- [13] J. Huang, S. Virji, B.H. Weiller, R.B. Kaner, *J. Am. Chem. Soc.* 125 (2003) 314.
- [14] J. Huang, R.B. Kaner, *J. Am. Chem. Soc.* 126 (2004) 851.
- [15] D.D. Sawall, R.M. Villahermosa, R.A. Lipeles, A.R. Hopkins, *Chem. Mater.* 16 (2004) 1606.
- [16] X. Zhang, W.J. Goux, S.K. Manohar, *J. Am. Chem. Soc.* 126 (2004) 4502.
- [17] X. Zhang, S.K. Manohar, *J. Am. Chem. Soc.* 126 (2004) 12714.
- [18] W. Li, H.L. Wang, *J. Am. Chem. Soc.* 126 (2004) 2278.
- [19] J. Duchet, R. Legras, S. Demoustier-Champagne, *Synth. Met.* 98 (1998) 113.
- [20] M. Trchova, I. Sedenkova, J. Stejskal, *Synth. Met.* 154 (2005) 1.