Novel Solid-State and Template-Free Synthesis of Branched Polyaniline Nanofibers

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Polyaniline is one of the most remarkable among the large family of conductive polymers and has been studied and used in many fields,[1] such as anticorrosion and antistatic coatings, batteries, and sensors. Considerable efforts have been made on the synthesis of polyaniline nanomaterials. [2–16] Although conductive polymers can be prepared by electropolymerization methods, [17,18] the most common route is chemical oxidation polymerization from monomers in solutions. By carefully controlling the experimental conditions to adjust the nucleation and growth of the polymer, researchers have recently sucessfully developed several typical oxidation polymerization methods to fabricate polyaniline nanofibers in solution without using any surfactant or hard template, such as interfacial polymerization,[3] rapidly mixed reaction,[4] and dilute polymerization.[5] However, in other solution methods, to control the size and shape of the polymer, at least one of the structure controlling materials, e.g., hard template, [6] special surfactant and dopants, [8–13] and/or organic solvent, have been used in the process. As the removal of the structure-determinant materials introduces additional work in those solution methods, when considering the economic and "green" factors of fabrication, a simpler and environmentally more friendly method to prepare polymer nanomaterials is highly desirable.

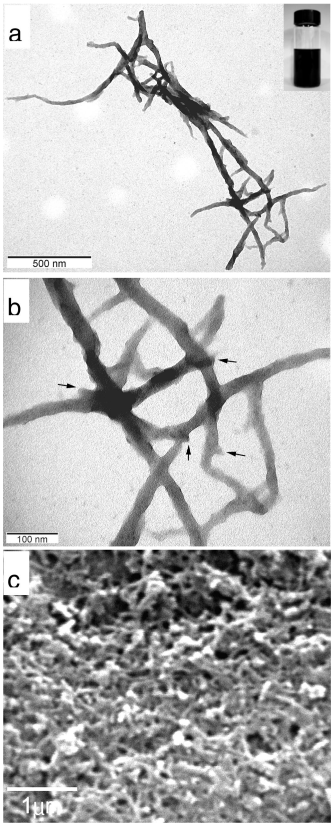

Figure 1. (a,b) TEM images and (c) SEM image of the products. Inset: the product in ethanol after 7 days.

The solid-state chemical reaction is proven to be an efficient method to prepare different nanomaterials. [19–21] As the liquid monomer aniline forms solid salts with mineral acids, e.g., aniline hydrochloride (mp. 196−198 °C), it is possible to use room temperature solid-state polymerization of a solid anilinium salt to prepare polyaniline nanomaterials. In this Communication, a facile solid-state mechanochemical route for branched polyaniline nanofibers without using any additional templates, organic acid, and surfactants was demonstrated (see the expermimental details in the Supporting Information).

The TEM image (Figure 1a) reveals that the polyaniline product consists of a large quantity of highly branched polyaniline nanofibers rather than isolated fibers or bundles of single fibers. Most short polyaniline nanofibers grow from each other forming a coralloid treelike superstructure. The diameters of most fibers are less than 40 nm. Although polyaniline dendrite made up of nanofibers or nanotubes has been reported very recently, the synthesis of the branched

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polyaniline fibers here is different. The previously reported polyaniline dendrites are prepared in a solution with the assistance of a special organic acid[12] and surfactant,[13] or synthesized in a surfactant gel, [7] whereas ours are prepared with a solid-state reaction simply between the monomer and oxidants. Moreover, the diameter of most dendritic fibers is obviously thinner than the reported values (>40 nm) in references.[7,13] High-magnification TEM image (Figure 1b) shows that the branches are always thinner than those branches on which they are growing from, indicating a hierarchical structure of the product. There are some asperities and nanorods on the surface of the nanofibers, (see arrows), which could be future branches at the very early stage. SEM image (Figure 1c) shows the entangled nanofibers predominantly in the product accompanied by a few small particles. Although the polymerization of aniline can take place in the solid state by freezing the reaction mixture,[22,23] or mechanochemical polymerization of aniline or its derivatives using ammonium peroxydisulfate (APS) [24–28] or polyoxometalate oxidant, [29] no dendritic polymer nanofiber product has been reported in these methods. Indeed, among these methods,[22–29] fiberlike polyaniline was obtained only in the presence of an organo-acid,[25] where the product was highly aggregated particles with their surfaces showing a fibrillar morphology. So, $FeCl_3 \cdot 6H_2O$ used in the present reaction must have played an important role in the formation of branched nanofibers. The synthesis yield (~8%) is comparable to that of the solution interfacial polymerization method.[3] EDX analysis shows a small amount of chlorine element in the product, whereas no iron element was detected, indicating doping of HCl of the product. This is different from the report of doping polyaniline base with $FeCl_3$ in nitromethane,[30] as our product is polymerized from aniline hydrochloride.

The prepared polyaniline branched nanofibers were easily dispersed in common solvents, such as deionized water, ethanol and acetone with the assistance of ultrasonics. The resulting suspensions were stable for several minutes to days, followed by agglomeration and precipitation. The stable time of the suspensions varied with different solvents used. The inset photo in Figure 1a shows the suspension of the product in ethanol for 7 days. It is well-known that $\pi-\pi$ interactions often exist in π-conjugated materials, such as polyaniline and carbon nanotubes. Considering the abundance of π-type bonds, polyaniline nanofibers should self-assemble into bundles through $\pi-\pi$ interactions between the fibers and precipitate from the solution, just like the case of unmodified carbon nanotubes. However, the stereohindrance effect of the branched structure prevents the nanofibers from self-assembly into bundles and retains high surface area with the solvents. Therefore, the good dispersability of nanofibers might be a result of their branched structure. Moreover, after being cast into a film from the suspension, it is difficult to redisperse the nanofibers in the solvent, even with ultrasonics, implying strong interactions and entanglement among the branched nanofibers in the film. All these indicate that the branched structure has increased the processibility of the polyaniline nanofibers.

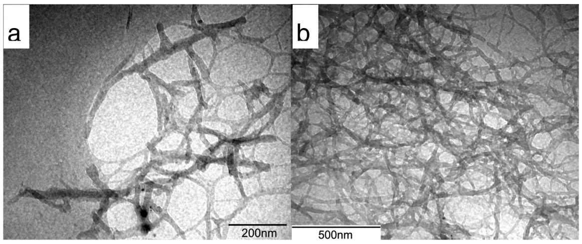

Figure 2. TEM micrographs of the products obtained (a) after grinding for 40 min and $[FeCl_3 \cdot 6H_2O]$:[aniline] = 1:1; and (b) after grinding for 4 h and $[FeCl_3 \cdot 6H_2O]$:[aniline] = 2:1.

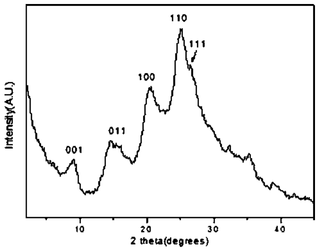

Figure 3. X-ray diffraction pattern of the product.

The effects of reaction time and concentration of the oxidant on the morphology of the products were examined. Changing the ratio between oxidant and monomer was found to have little influence on the morphology of the polymer nanostructures. When the $[FeCl_3 \cdot 6H_2O]$:[aniline] ratio was increased from 1:1 to 2:1, the diameter and dendrite structure of the nanofibers did not change much, as shown in Figure 2a and Figure 1, respectively. Increasing the reaction time from 40 min to 4 h also had no significant effect on the branched structure of the nanofibers (Figure 2b). Furthermore, the morphology did not change significantly when the fibers were dedoped with 0.1mol/L NH_4OH.

Figure 3 shows the XRD patterns of the resultant polyaniline. Three broad peaks centered at $2\theta = 9$, 14.6, and 20.3° and a sharp peak at $2\theta = 25.3°$ together with a weak peak at 26.5° are observed, indicating that the resulting polymer is in the form of a highly doped emeraldine salt and has good crystallinity.[24,31] Three stages of weight loss appeared in the DTG curve (Figure 4) of the product below 600 °C. The first stage below 140 °C was mainly caused by the removal of free water, whereas the second stage between 140 and 350 °C was ascribed to the elimination of dopants (mainly HCl), and the third stage around 500 °C was caused

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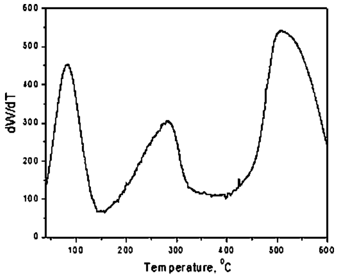

Figure 4. DTG of the branched polyaniline nanofibers.

by the thermal decomposition of the polyaniline backbone chains.[32] Moreover, in the FT-IR spectrum of the product, characteristic peaks of the C═C stretching vibration mode of the quinonoid and benzenoid rings appeared at about 1480 and 1560 cm^{-1},[33,34] respectively, and the former peak is stronger than the latter, showing that the prepared dendritic polyaniline nanofibers are an emeraldine salt. These results are similar to those prepared in solution[35] and confirm the emeraldine salt form of the product.

Appropriate static conditions of the solution are beneficial to formation of polyaniline nanofibers with previous solution methods.[36] However, solid state reaction cannot proceed successfully without grinding because of the limited reaction interfaces between the reactants. The temperature changes little when the mixture change its color from orange to green (indicating polymerization of aniline and reduction of Fe^{3+}). Moreover, contrary to the obvious color change when using anilinium chloride as precursor, the mixture remains light orange even after grinding for 40 min when using anilinium sulfate as the reactant, indicating that occurrence of mechanochemical polymerization is difficult. These imply that the polyaniline growth mechanism in solid-state polymerization is different from that prepared with solution methods. In solid-state polymerization of polyaniline with $FeCl_3 \cdot 6H_2O$ as the oxidant, HCl and free water are produced, which continually afford an aqueous HCl solution that benefits the self-catalyzed polymerization of polyaniline at the solution/solid interface. Also, because of the low melting point of $FeCl_3 \cdot 6H_2O$, that is, 37 °C, it is easily melted and mixed with the monomer under mechanical grinding at room temperature, which was confirmed by the fact that the reaction mixture became a slurry after 8 min. All these ensure polyaniline nanofibers are produced successfully in the solid state mixture. It is noted that compared with $FeCl_3 \cdot 6H_2O$, the normally used APS contains no crystalline water and has too high a melting point (120 °C).

At present, the forming mechanism of dendritic polyaniline nanostructure is still unclear. However, the formation of branched nanofibers is probably related to the mechanochemical oxidation polymerization process and linear nature of the polyaniline molecule chains. It is known that the structure of products depends on the rate of nucleation and growth of the ultimate products in solid-state reaction.[21] According to the nucleation theory, [5,37] the nanofibers formed initially may serve as nucleation sites for additional fibers (that is, secondary nucleation). For polymer forming during grinding of the reactive mixture, because there is competition between directional 1D growth and normal grain growth, a few active nucleation centers commence on some specific points of previously formed nanofibers, which may result from the limited solid/liquid interfaces in the solid reaction system. Subsequent growth of polyaniline on these points leads to the formation of polyaniline nanorods and branches on the fibers. Such small asperities, which may act as active sites for nucleation and further growth of secondary nanofibers, are identified by arrows in Figure 1b.

To conclude, a simple and practical solid-state reaction method to synthesize branched polyaniline nanofibers was demonstrated without using any surfactant and organic solvent. The unique structure and good dispersion ability of our prepared branched polyaniline nanofibers in various systems will provide potential applications as electrode materials and novel conductive fillers in nanocomposites. Although solid state reaction has been used widely in synthesis of inorganic nanocrystals, few studies have been conducted using this method to fabricate polymer nanomaterials. This research has extended current solution-based methods to the solid-state reaction and provides a simpler route to process polymer nanomaterials.

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Supporting Information Available: Experimental details (PDF). The material is available free of charge via the Internet at http://pubs.acs.org.

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