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Polyaniline Hierarchical Structures Synthesized in Aqueous Solution: Micromats of Nanofibers

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Polyaniline (PANI) nanomaterials have gained significant interest in recent times because of their unique electronic properties, simple synthesis process, environmental stability and low cost,[1] the morphology of PANI has been widely studied due to its strong influence on the properties and applications. So far, various methods have been developed for synthesizing one-dimensional (1D) PANI nanostructure, such as polymerization of aniline with "hard" templates[2] or in the presence of "soft" templates, such as micelles,[3] surfactants,[4] liquid crystals,[5] nanowire "seeds",[6] and inverse microemulsions,[7] or by some new synthetic strategies, such as rapid mixing reaction,[8] interfacial polymerization,[9] and dilute polymerization.[10] Very recently, it has been reported that the oxidation polymerization in aqueous solution in the absence of any doping acid produced PANI nanotubes with aniline concentration 0.2 M.[11,12] In this communication, we report that when the oxidation polymerization is carried out in dilute aniline aqueous solution (such as 16 mM), a novel micromat of PANI nanofibers with hierarchical structure can be obtained.

As well-known, the hierarchical assembly of conducting polymer nano building blocks is an key step toward constructing future nanoelectronic devices.[13] Although there have been a few reports on the preparation of PANI aligned nanostructure,[14,15] the studies dealing with the fabrication of PANI hierarchical structure based on 1D structure are still lacking. What is more, this preparing system is very economical and convenient from the chemical point of view because it includes just two reactants and can be performed at room temperature. The sizes and morphologies of PANI micromats have been controlled by changing experimental parameters in this research.

In a typical synthesis, aniline (0.0297 g) was dissolved in deionized water (20 mL) with magnetic stirring at room temperature for 10 min. After that the aqueous solution of ammonium persulfate (APS) was added to the above mixture in one portion. The resulting solution was stirred for another 0.5 min to ensure complete mixing, and then the reaction was allowed to proceed without agitation for 12 h at room temperature. Finally, the product was washed with deionized water until the filtrate became colorless and then dried in a vacuum at 60 °C for 24 h.

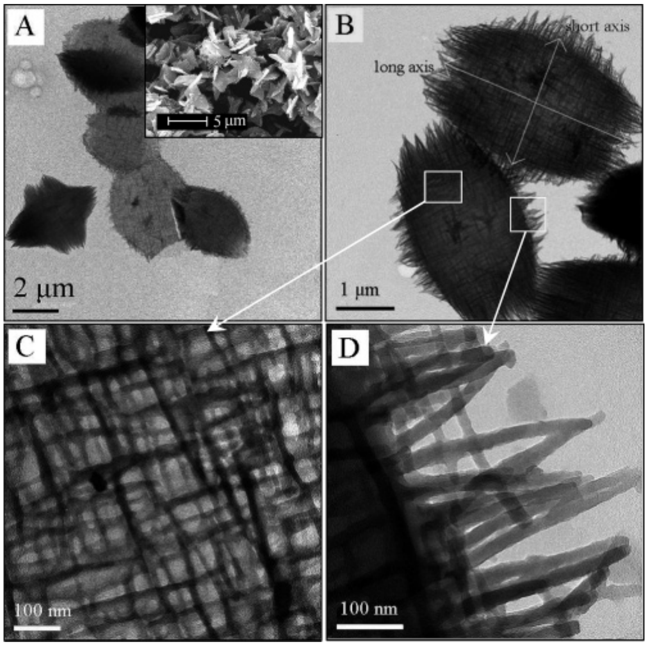

Figure 1. (A−D) TEM images of micromats of PANI nanofibers synthesized in aqueous solution. The inset in part A shows the SEM image of PANI micromats. Synthetic conditions: [aniline] = 16 mM; [APS]/[aniline] = 1.0:1; 25 °C.

Figure 1 presents the typical transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of the obtained micromats of PANI nanofibers. The low magnification image (Figure 1A) clearly reveals that the product has uniform micromat morphology (inset) and is composed of shuttlelike micromats and crossed shuttlelike micromats which are cross-linked by two quasi-vertical shuttlelike structures. Figure 1B further displays the cross-linked structure of PANI nanofibers on the micromats with about 4 μm in long axis and 2.5 μm in short axis (as marked in this figure). From the magnified TEM images in Figure 1, parts C and D, we can see evidently that the surface of micromat is knitted by nanofibers with an average diameter of 20 nm, while its margin consists of quasi-parallel nanofibers with a few crossed fibers.

The growth processes of PANI micromats in water are followed by examining the morphological development of products (Figure 2A). It is found that the offspring produced with reaction time 0.5 h is platelike structures composed of phenazine units (their FTIR characteristic bands at 1620, 1415, and 1207 cm^{-1},[16] in Figure 2B) and possesses good crystallinity (Figure 2C). Then, PANI nanofibers grow gradually on top of the initially formed platelets (marked by arrows) at reaction time 1.5 h, and finally, complete PANI micromats are constructed for the 3 h reaction, accompanied by the decreasing proportion of phenazine units (reflected by FTIR spectra of Figure 2B) and the decreasing crystallinity (observed from Figure 2C). We deduce the polymerization processes of aniline and propose a possible growth mechanism of PANI micromats as follows: When aniline is added into water, the hydrolyzation of part of aniline results in the coexistence of neutral molecule and anilinium cation.[16] After the addition of oxidant, neutral molecules are first oxidized to yield *ortho*-coupled units which can be further oxidized to phenazine units.[17] Such phenazine units precipitate as platelike crystallite due to their flat structures and low solubility,[18] simultaneously the phenazine units in solution also initiates the propagation of oligomer chains by linking anilinium cations in the *para*-position.[16] The resulting oligomer is thus expected to have a phenazine head segment and a tail of *para*-linked aniline constitutional units containing quinoid structures which are formed by the two-electron oxidation with APS.[17] After that, such hydrophobic oligomers can adsorb on the surface of platelike crystallite through their terminal phenazine units,[12,16] and the cross-linking reaction proceeds at imine nitrogen of one oligomer chain adsorbed,

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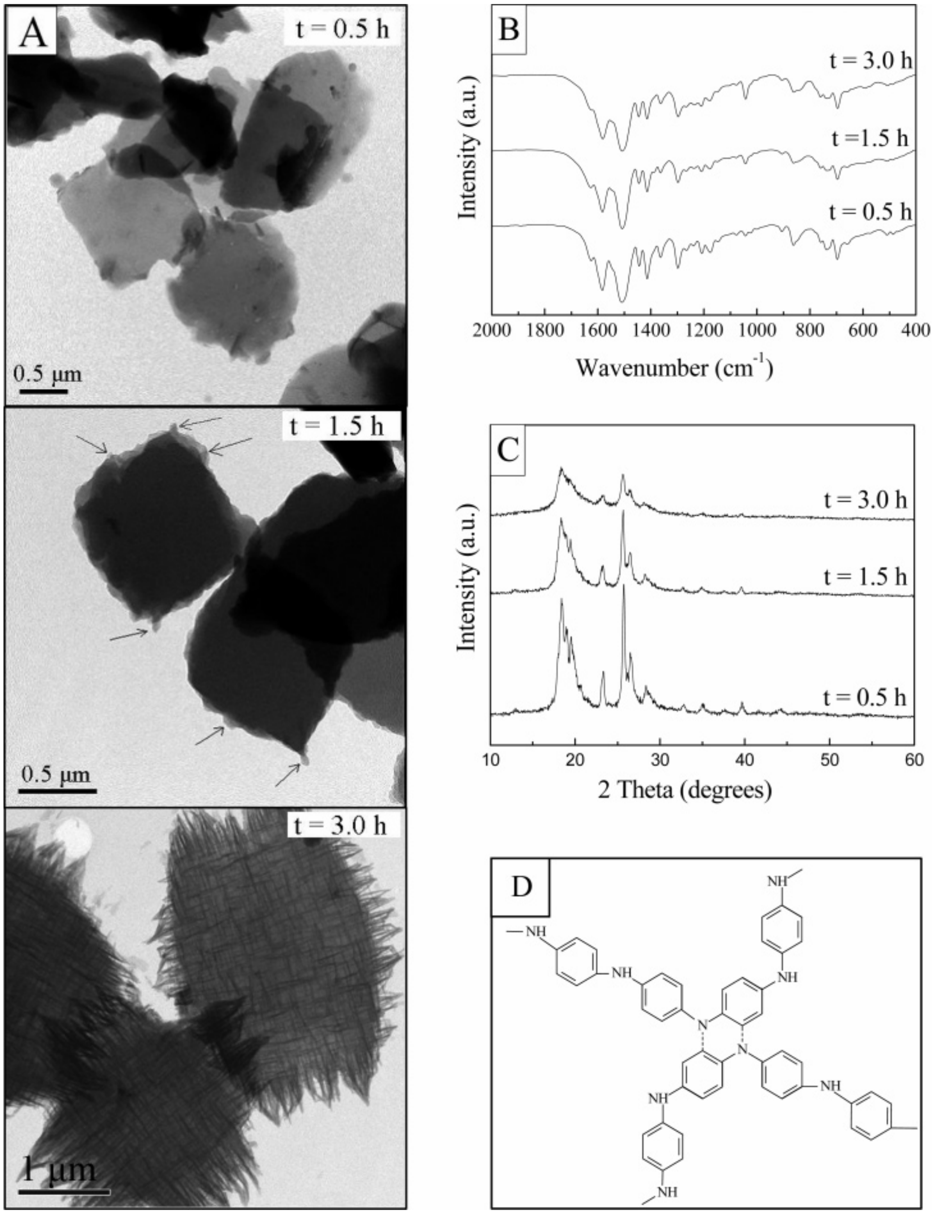

Figure 2. (A) TEM images, (B) FTIR spectra, and (C) XRD patterns of products synthesized at different reaction times (synthetic conditions: [aniline] = 16 mM; [APS]/[aniline] = 1.0:1; 25 °C); (D) Illustration of cross-linked PANI chain structure. The dashed line represents the new bond formed by the cross-linking reaction between oligomer chains.

forming a chemical bond with the quinoid ring of another chain and producing a 2D cross-linked polymer structure (Figure 2D).[19] Such a cross-linked structure can be confirmed by the FTIR spectra in Figure 2B with the band at 1040 cm^{-1} corresponding to 1,2,4-substitution of aromatic rings[20] which appears with nanofibers for 1.5 h reaction, and its intensity is strengthened as the growth of the crossed nanofibers for another 1.5 h. Therefore, it is reasonable to believe it is the cross-linking reaction between oligomer chains that guides the growth of polymer chains along two directions, inducing the crossed structure of final nanofibers. Moreover, the pH value of solution is found to decrease as aniline polymerizes (Figure S1), and it reaches 3.2 when the polymerization time is 1.5 h. According to the literature, aniline molecule exists as anilinium cation when the pH value is lower than 4,[16] and the nanofibers of PANI seem to be an intrinsic morphological unit with the polymerization of anilinium cations.[8−10] Therefore, it is not surprising that the polymerization for 1.5 h of reaction (pH < 4) generates nanofibers (Figure 2A). Simultaneously, the platelets formed initially may provide a template for the growth of nanofibers, resulting in PANI micromats covered with crossed nanofibers.

Interestingly, the concentration of aniline is found have significant influence on the sizes of PANI micromats and nanofibers as building blocks. As shown in Figure 3A, when the concentration of aniline is low (e.g., 4 mM), only relatively small-sized micromats with 3.0−3.5 μm in long axis and about 1.8 μm in short axis is obtained. If the concentration of aniline is up to 12 mM, the micromats of PANI nanofibers are estimated to 3.5 μm in long axis and 2.2 μm in short axis (Figure 3B). When the concentration of aniline increases to 20 mM (Figure 3 C), the average size of long axis of micromats is 4 μm, and their short axis are about 3 μm. However, the large-sized micromats (4−6 μm in sizes) are observed accompanied by individual nanofibers (*ca.* 100 nm in diameter) at the aniline concentration of 28 mM (Figure 3D). As shown in the insets in Figure 2, the diameters of nanofibers as building blocks increase from 15 to 100 nm with the increasing concentration of aniline from 4 to 28 mM.

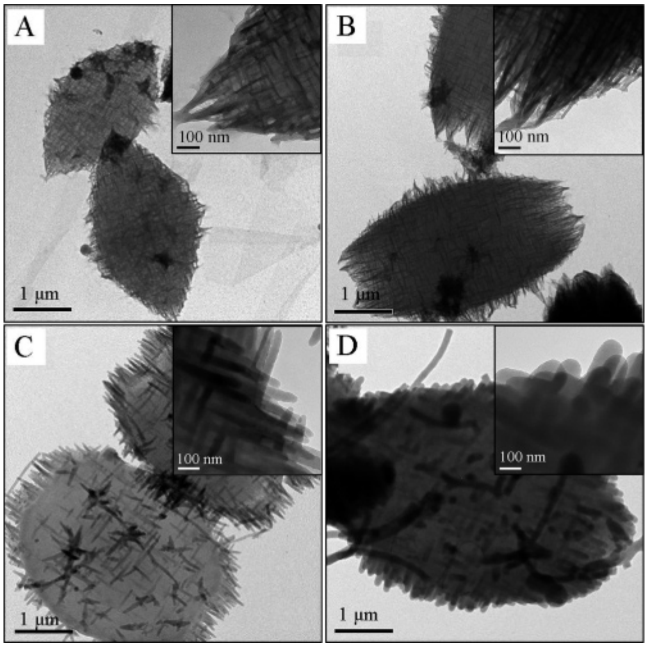

Figure 3. TEM images of micromats of PANI nanofibers synthesized in aqueous solution with different concentrations of aniline (mM): (A) 4; (B) 12; (C) 20; (D) 28. Other synthetic conditions: [APS]/[aniline] = 1.0:1; 25 °C. Insets of parts A−D show networklike structures of PANI nanofibers on these micromats.

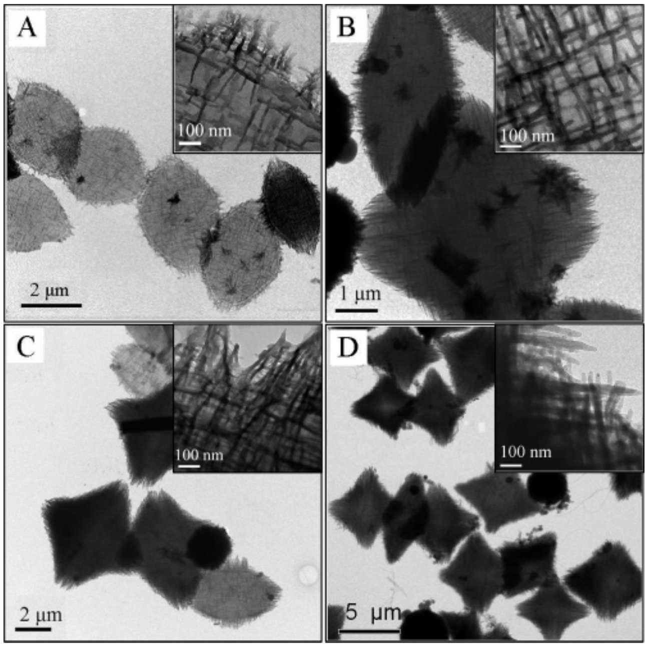

Figure 4. TEM images of micromats of PANI nanofibers synthesized in aqueous solution with different [APS]/[aniline] molar ratios: (A) 0.5:1; (B) 0.8:1; (C) 1.2:1; (D) 1.5:1. Other synthetic conditions: [aniline] = 16 mM; 25 °C. Insets of parts A−D show networklike structures of PANI nanofibers on these micromats.

Our preliminary experiments indicate that the [APS]/[aniline] ratio evidently influences the morphology of PANI. Figure 4A shows that the uniform shuttlelike micromats of PANI nanofibers can be obtained when the [APS]/[aniline] ratio is 0.5:1. Comparing insets in Figure 4, parts A and B, it can be clearly seen that the node density of networklike nanofibers on the micromats thickens as the [APS]/[aniline] ratio increase from 0.5:1 to 0.8:1. A high density of oxidation centers is generated at a high concentration of APS, which is favorable for the two-electron oxidation of oligomer with APS to produce quinoid structures.[17] So that the proportion of quinoid structures in chain increases with the concentration of APS, which provides the more chances for the cross-linking reaction between imines nitrogen of one chain and quinoid ring of another chain.[19] Therefore, the frequent cross-linking reactions results in the more node of networklike nanofibers on the micromats. Surprisingly, it is also found that the shuttlelike micromats of PANI nanofibers decrease while crossed shuttlelike structures increase with the increasing [APS]/[aniline] ratio. As shown in Figure 4A, the majority morphology of product is shuttlelike micromats with the [APS]/[aniline] ratio of 0.5:1, while the mixture of shuttlelike and crossed shuttlelike structures can be observed when the [APS]/[aniline] ratio is between 0.8:1 and 1.2:1 (Figure 4, parts B and C). However, crossed shuttlelike micromats of PANI nanofibers become dominating at the [APS]/[aniline] ratio of 1.5:1 (Figure 4D). And insets in Figure 4, parts C and D, display the networklike structures of PANI nanofibers on the edge of crossed shuttlelike micromats.

In conclusion, micromats of PANI nanofibers with hierarchical structures have been prepared for the first time in water. The concentration of aniline and the [APS]/[aniline] ratio can be employed to adjust the size and morphology of PANI micromats. The result of UV/vis spectra has indicated that the PANI synthesized in aqueous solution can still be reversibly doped and dedoped (Figure S2). The PANI micromats have potential for incorporation into functional electronic, *opto*-electronic, or sensing devices, which could lead to extreme miniaturization and enhanced performance.

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Supporting Information Available: Text discussing the chemical structure characterization and Figure S1, a plot showing the pH value of solution decreasing as aniline polymerizes, and Figure S2, UV/vis spectra of PANI micromats. This material is available free of charge via the Internet at http://pubs.acs.org.

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