

Self-Assembled Polyaniline Nanofibers/Nanotubes

Nan-Rong Chiou,^{†,‡} L. James Lee,[†] and
Arthur J. Epstein^{*,‡,§}

Department of Chemical and Biomolecular Engineering,
The Ohio State University, Columbus, Ohio 43210-1180,
Department of Physics, The Ohio State University,
Columbus, Ohio 43210-1117, and Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210-1185

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Polyaniline can be prepared by either chemical or electrochemical oxidative polymerization.¹ Since these early works several chemical methods were reported for synthesis of polyaniline nanofibers/nanotubes.² In these methods, in general, it is required to polymerize aniline in a medium comprised of a protonic acid which simultaneously acts as a dopant to protonate as-synthesized polyaniline resulting in conductive emeraldine salt. Recently, polyaniline has been prepared directly from the aqueous medium without using any protonic acid in the beginning of polymerization.³ However, the morphology of polyaniline powder obtained shows mainly short solid/hollow nanorods including some non-fibrous particulates.⁴ Anisotropic growth (one-dimensional, 1-D, elongation) is suppressed in such a system. Herein, we report for the first time a successful synthesis of the highly uniform, relatively long nanofibers/nanotubes of polyaniline via a self-assembly process assisted by the presence of excess oxidant ((NH₄)₂S₂O₈; ammonium persulfate; APS) without the use of any acid in the initial step.

The scanning electron microscopy (SEM) images (Figure 1a) show that polyaniline synthesized utilizing excess APS is composed of two different sizes of the nanofibers with average diameters of ~26 nm (Figure 1a, inset) and ~120 nm (Figure 1a), respectively, confirmed by the transmission electron microscopy (TEM) images (Figure 1b–d). In addition to solid nanofibers, some hollow nanofibers (i.e., nanotubes) can be found with their wall thickness ranging from 35 nm to 40 nm (Figures 1b,c). The diameters of nanofibers/nanotubes described here are based on multiple TEM measurements with statistical analyses in different areas. The lengths of polyaniline nanofibers/nanotubes with larger diameters are up to several micrometers. The surfaces of the nanofibers/nanotubes are not smooth, showing asperities along the fibers/tubes (Figure 1c,d). The fibrous/tubular morphology is reproducible for the same polymerization conditions. Besides the relatively long nanofibers/nanotubes, a few micro-/nanospheres (Figure 1e, inset) and granular/flake-like particulates appear in the product (Figure 1e). Such microsphere structure is quite similar to that of the previous report.⁵ This may result from the decreasing pH during our synthesis. Interestingly, the individual nanofiber/nanotube can be easily isolated from the agglomeration as the sample is dispersed in a large amount of water or methanol.

After purification and redoping by 1 M HCl(aq), doped polyaniline nanostructures present the characteristic absorption bands of emeraldine salt (ca. 320 nm, 420 nm, and 980 nm with a long tail to the IR; Supporting Information, Figure S1a, solid line).² Adding five droplets of 30% (w/w) NH₄OH(aq) to the above dispersion of doped polyaniline nanostructures introduces the formation of an absorption band of approximately 650 nm, simultaneously resulting in the disappearance of two absorption bands at approximately 420 nm and 980 nm. The long tail to the IR of the 980 nm absorption band also disappears (Supporting Information, Figure S1a, dashed line). The two strong absorption bands at approximately 320 nm and 650 nm are attributed to the formation of emeraldine base.² The UV/vis absorption patterns of polyaniline nanostructures obtained are consistent with previously reported results for polyaniline powders, thin films, nanotubes, and nanofibers.² The Fourier transform infrared (FT-IR) spectrum of doped polyaniline reported here (on KBr; measured under vacuum; Supporting Information, Figure S1b) shows the characteristic absorption bands of doped polyaniline salt with the following five major vibrational bands: 1560, 1480, 1290, 1128, and 792 cm⁻¹.⁶ Compared to emeraldine base^{6a} and emeraldine salt,^{6b} the additional band at 1035 cm⁻¹ is correlated with sulfate ions resulting from the (NH₄)₂S₂O₈ oxidant.

We determined that the pressed pellet room temperature direct current conductivity is ~4.3 × 10⁻³ S/cm. Comparing

* Corresponding author. E-mail: epstein@mps.ohio-state.edu.

[†] Department of Chemical and Biomolecular Engineering.

[‡] Department of Physics.

[§] Department of Chemistry.

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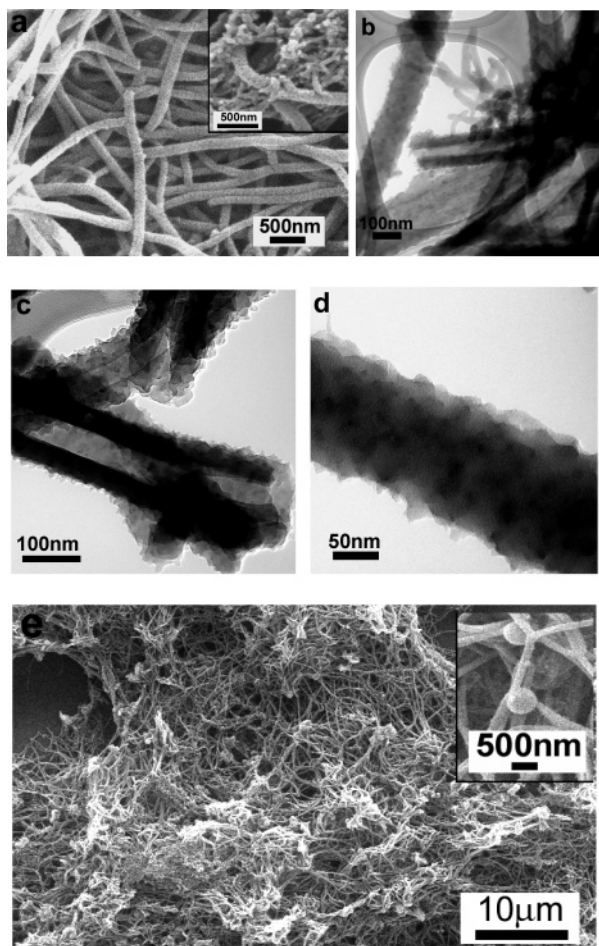


Figure 1. Polyaniline synthesized by self-assembly in the presence of excess APS without the use of any acid in the beginning of polymerization. (a) SEM images show the morphology of the nanofibers. (The inset shows nanofibers with the smaller diameters.) (b) TEM image shows that as-synthesized polyaniline consists of the nanofibers (with two different nanosizes) and the nanotubes. (c and d) TEM images show the asperities along the surfaces of polyaniline nanofibers and nanotubes. (e) SEM image at low magnification shows highly uniform, relatively long nanofibers/nanotubes. (The inset shows the micro-/nanospheres appearing in the sample.)

to results reported for polyaniline nanofibers,^{2a-c,g} such lower conductivity may be attributed to the lower doping level resulting from the purification by methanol. However, the $\sim 4.3 \times 10^{-3}$ S/cm value is comparable to the conductivity reported for polyaniline nanotubes synthesized using surfactants.^{2f,h-j}

A recent study of the formation of polyaniline nanofibers proposed a model based on the role of anilinium–persulfate ion clusters.⁷ However, this model does not account for our results. In our case, the unprotonated form of aniline ($pK_a = 4.6$) dissolved in deionized water ($pH \sim 5.8$) does not interact with $(NH_4)_2S_2O_8$ oxidant to form the $(C_6H_5-NH_3)_2S_2O_8$ complex within the induction time. According to Manohar et al., under these conditions only irregular-shaped polyaniline could be produced.⁷ In contrast, polyaniline nanofibers/nanotubes dominate the morphology in our system.

We propose here a mechanism for the formation of polyaniline nanofibers/nanotubes synthesized in the presence

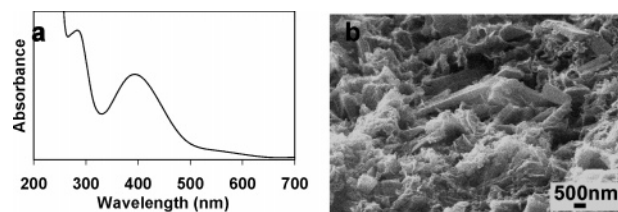


Figure 2. (a) UV/vis spectrum and (b) SEM image taken from the precipitate isolated in the early stage of self-assembly at 5 min.

of excess oxidant. Aniline is oxidized by $(NH_4)_2S_2O_8$ to form reactive aniline cation–radicals, simultaneously producing H_2SO_4 by the reduction of $(NH_4)_2S_2O_8$.^{3,5} This lowers the pH in the reaction, resulting in the protonation of as-synthesized polyaniline (final product). Two initial formed aniline cation–radicals combine into a dimer which is further oxidized by APS to form a dimer cation–radical. Such dimer cation–radicals could act as surfactants to template the formation of nanostructures. Indeed, we terminate the reaction in the early stage of polymerization (~ 5 min), and the isolated precipitate has the typical absorption patterns of aniline dimers (Figure 2a).^{3a,5,8} SEM shows such early isolated precipitate consisting of flake-like/rectangle-like non-fibrous morphology (Figure 2b). This is analogous to the previous reports.^{2i,4}

The dimer cation–radical surfactant could aggregate to form different sizes and types of micelles. The shape of the micelle including spheres, cylinders, and interconnected networks strongly depends on the surfactant concentration and interaction between surfactants and counterions.⁹ In a self-assembly process, excess oxidant can benefit the formation of interconnected network-like nanofibers/nanotubes. Only excess APS (for example, molar ratio of aniline to $(NH_4)_2S_2O_8 = 0.274$) produces longer and more uniform nanofibers/nanotubes although some nanofibers still could be found spontaneously for the molar ratios of aniline to APS greater than or equal to 1 (Supporting Information, Figure S2). Non-fibrous particulates in nano-/micrometer sizes gradually dominate the morphology when the molar ratio of aniline to APS increases (Supporting Information, Figure S2d).

Excess APS initiator rapidly induces the formation of dimer cation–radicals (dimer surfactant) before polymerization resulting in the increase of the surfactant concentration in an aqueous solution. As supported in ref 10, this leads dimer cation–radical surfactant to transform from spherical micelles into the fibrous and/or tubular structured micelles for the later formation of the nanofibers and/or nanotubes. In other words, it is necessary to add an appropriate amount of surfactant and counterions (e.g., acid, ionic species, or solvent) to assist dimer micelles to aggregate into fibrous and/or tubular structures if the number of the dimer cation–radicals present are insufficient in the synthesis. Indeed, previous reports support our hypothesis.^{2,10} In contrast, if the surfactant or counterion added to aniline polymerization has an inappropriate concentration, the structure of the resulting

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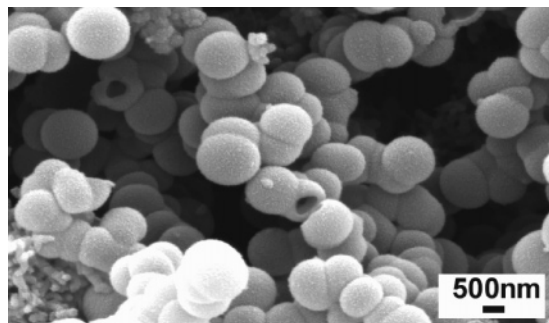


Figure 3. SEM image of polyaniline synthesized by self-assembly in the presence of a small amount of 2-hydroxy-3-naphthoic acid. Polymerization conditions: [aniline] = 0.128 M, [APS] = 0.128 M, and [2-hydroxy-3-naphthoic acid] = 0.0128 M.

dimer micelles could be unchanged or remarkably altered into other possible shapes. For example, the morphology of polyaniline dramatically changes from 1-D nanofibers/nanotubes to three-dimensional (3-D) hollow micro-/nanospheres when a small amount of 2-hydroxy-3-naphthoic acid is present (Figure 3). This is also consistent with previous studies.^{2f,h,i} However, there is no apparent difference for the morphology of polyaniline synthesized in the presence of a small amount of added H₂SO₄ (Supporting Information, Figure S3). This also confirms that 1-D elongation results from excess APS, not from H₂SO₄ produced by APS. Now,

it is clear that polyaniline self-assembles to form elongated 1-D nanostructures under specific synthesis conditions. Adding surfactant, solvent, acid, and/or ionic species only alters the micelle structure of aniline dimer cation–radicals. Under specific conditions, polyaniline nanostructures can be tuned into different shapes, depending on the condition of the micelle formation.

In summary, we use a different synthesis route to control the formation of polyaniline nanostructures. We demonstrated for the first time that excess APS preferentially forms highly uniform, extra long nanofibers/nanotubes. This may be accounted for by the formation of aniline dimer cation–radicals which could act as effective surfactants to shape the polyaniline morphology. On the basis of this hypothesis, polyaniline nanostructures could be altered from elongated 1-D nanofibers/nanotubes to 3-D hollow micro-/nanospheres in the presence of surfactant or counterion additives.

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Supporting Information Available: Synthetic details and additional SEM images (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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