A General Chemical Route to Polyaniline Nanofibers

Jiaxing Huang and Richard B. Kaner*

Contribution from the Department of Chemistry and Biochemistry and California NanoSystems Institute, University of California, Los Angeles, California 90095-1569

Received July 9, 2003; E-mail: kaner@chem.ucla.edu.

Abstract: Uniform polyaniline nanofibers readily form using interfacial polymerization without the need for templates or functional dopants. The average diameter of the nanofibers can be tuned from 30 nm using hydrochloric acid to 120 nm using perchloric acid as observed via both scanning and transmission electron microscopy. When camphorsulfonic acid is employed, 50 nm average diameter fibers form. The measured Brunauer−Emmett−Teller surface area of the nanofibers increases as the average diameter decreases. Further characterization including molecular weight, optical spectroscopy, and electrical conductivity are presented. Interfacial polymerization is shown to be readily scalable to produce bulk quantities of nanofibers.

Introduction

Polyaniline is unique among the family of conjugated polymers since its doping level can be readily controlled through an acid doping/base dedoping process.[1] Since polyaniline's conducting properties were rediscovered in the early 1980s, it has been extensively studied for many potential applications including lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings, and sensors.[2] Nanostructured polyaniline (nanorods/-wires/-fibers) offers the possibility of enhanced performance wherever a high interfacial area between polyaniline and its environment is important. For example, in sensor applications, nanostructured polyaniline has greater sensitivity and faster time response relative to its conventional bulk counterpart due to higher effective surface area and shorter penetration depth for target molecules.[3] However, such sensors[3,4] have not been widely exploited, likely due to the lack of facile and reliable methods for making high-quality conducting polymer nanostructures.

The classical chemical synthesis of polyaniline uses aniline, an oxidant and a strong mineral acid dopant.[1] Polyaniline nanotubes or nanofibers with diameters < 100 nm can be made by template-guided polymerization within channels of zeolites[5] or nanoporous membranes.[6−8] Adding structural directing molecules such as surfactants[9] or polyelectrolytes[10] to the chemical polymerization bath is another way to obtain polyaniline nanostructures. When organic dopants with surfactant functionalities are used, emulsions or micelles can be formed leading to microtubes, -fibers, or -rodlike structures.[11−15] However, if polyaniline nanostructures with diameters ≤ 100 nm are desired, then very complex dopants with bulky side groups are needed, such as sulfonated naphthalene derivatives,[11−13] fullerenes,[14] or dendrimers.[15] Since all these methods are dependent on either a template or a specific complex chemical reagent, post-synthetic treatments are needed to remove them from the products in order to recover the nanostructured polyaniline. Therefore developing syntheses that do not rely on templates, structural directing molecules, or specific dopants are important, especially for scaling up to produce large quantities of nanostructured materials. Electrochemical polymerization[4,16] and some physical methods, such as electrospinning[17] and mechanical stretching[18] can also produce conducting polymer nanofibers without templates, but these materials have only been made on a very limited scale, such as films on an electrode surface.

Recently, using camphorsulfonic acid as the dopant in an interfacial polymerization route, we have successfully synthesized polyaniline nanofibers with diameters near 50 nm, which are among the smallest reported for polyaniline nanofibers and nanowires without using a template.[3] Here, we explore the interfacial polymerization method and demonstrate that it is a very general route to create polyaniline nanofibers. Interfacial polymerization does not depend on any specific template or dopant. High-quality polyaniline nanofibers are obtained even when common mineral acids, such as hydrochloric, sulfuric, or

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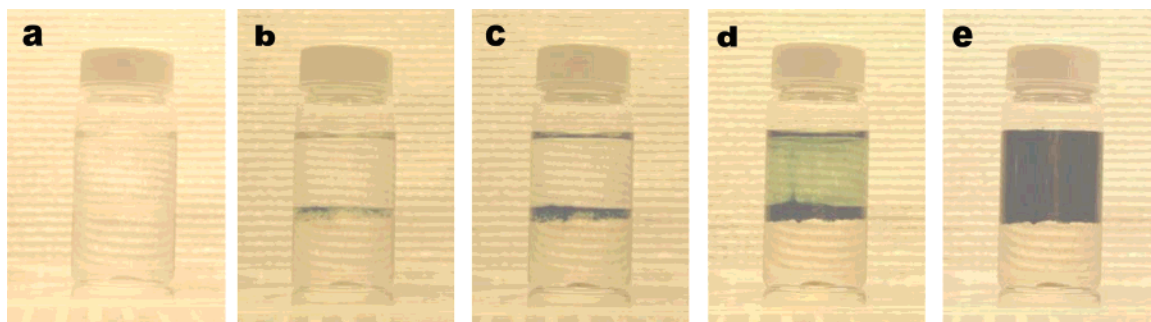(18) He, H. X.; Li, C. Z.; Tao, N. J. *Appl. Phys. Lett.* **2001**, *78*, 811−813.

Figure 1. Snapshots showing interfacial polymerization of aniline in a water/chloroform system. From a to e, the reaction times are 0, 1.5, 2.5, 4, and 10 min, respectively. The top layer is an aqueous solution of 1.0 M perchloric acid and ammonium peroxydisulfate; the bottom layer is aniline dissolved in the organic solvent chloroform.

nitric acid, are used as dopants. The syntheses can be accomplished in one pot with a wide choice of solvent pairs, acid dopants, and reagent concentrations over a broad range of temperatures.

Experimental Section

Synthesis. All chemicals were of analytical grade and used as received. Typically the interfacial reaction was performed in a 20 mL glass vial (Figure 1). A 3.2 mmol amount of aniline was dissolved in the organic phase (10 mL) such as hexane, benzene, toluene, xylene, diethyl ether, carbon disulfide, carbon tetrachloride, chloroform, *o*-dichlorobenzene, or methylene chloride. Ammonium peroxydisulfate (0.8 mmol) was dissolved in 10 mL of 1 M dopant acid solution. A great variety of dopant acids can be used, including hydrochloric, sulfuric, nitric, phosphoric, perchloric, acetic, formic, tartaric, camphorsulfonic, methylsulfonic, ethylsulfonic, or 4-toluenesulfonic acid, among others. In a 20 mL reaction vial, the concentration of aniline was varied from 0.032 to 0.32 M and the acid concentration was varied from 0.001 to 2.0 M to study their effects on the formation of nanofibers. Larger scale reactions were carried out in a 2 L beaker, where 1 L of aqueous solution with 0.5−1 M acid and 200 mL of organic solvent with 1.6 M aniline were used. In all reactions, the aniline to ammonium peroxydisulfate molar ratio was kept at 4 to 1.

Purification. To remove excess acid and byproducts from polymerization, the as-prepared polyaniline was purified by either dialysis (dialysis tube, 12 000−14 000 MW cutoff, Fisher Scientific) or filtration (Millipore, type GN, 0.20 μm filter). Doped nanofibers were obtained by dialyzing or washing with water; dedoped nanofibers were obtained by dialyzing or washing with 1 M NH$_3$·H$_2$O.

Microscopy. Samples for transmission electron microscopy (JEOL 100CX TEM) were prepared on Formvar-coated copper grids (Ted-Pella). Scanning electron microscopy (Philips XL 30 field emission SEM) samples were prepared on aluminum-foil-coated stages.

Spectroscopy. The absorption spectra of the nanofibers as aqueous dispersions were recorded on an HP 8453 spectrometer.

Molecular Weight. Molecular weight distributions of the nanofibers were measured by gel permeation chromatography (Shimadzu GPC), using a Polymer Laboratories PLgel MIXED-D 5 μm + guard column and an ELSD-LT evaporative light scattering detector. Nanofibers synthesized with HCl at room temperature were dedoped and dissolved in dimethylformamide, which was also used as the mobile phase (flow rate, 0.8 mL/min). The solutions were filtered with 0.20 μm syringe filters before being injected into the column. The column temperature was maintained at 40 °C. Polystyrene standards were used as the reference.

Surface Area. The surface area of the nanofibers was measured by nitrogen adsorption−desorption isotherms using the Brunauer−Emmett−Teller (BET) method (Micromeritics ASAP 2010). The samples were degassed under vacuum at room temperature before measurement.

Conductivity. Nanofibers made with 1.0 M HCl were filtered, washed with water, and dried under vacuum. The powder was pressed into pellets. The conductivity was calculated from the slope of an $I-V$ plot measured using a two-probe setup with an error of 5−10%.

Results and Discussion

Synthesis and Characterization. Interfacial polymerization is performed in an aqueous/organic biphasic system (Figure 1) with aniline dissolved in an organic solvent and the oxidant, ammonium peroxydisulfate, dissolved in an aqueous acid solution. A great variety of organic solvents can be used, including benzene, hexane, toluene, carbon tetrachloride, chloroform, methylene chloride, diethyl ether, carbon disulfide, or *o*-dichlorobenzene. However, the shape and size of the nanofibers do not appear to be affected by the solvent. Therefore, a less toxic organic solvent that is heavier than water, such as methylene chloride, is preferred due to safety considerations, since water can help to seal the organic vapor within the reaction vessel. The water layer is carefully spread onto an equal volume of the organic solvent, forming an aqueous/organic interface (Figure 1a). After a short induction period ranging from 30 s to several minutes depending on the acid used, green polyaniline appears at the interface (Figure 1b), migrating into the water phase (Figure 1c,d), and finally filling the entire water layer (Figure 1e). As the reaction proceeds, the color of the organic phase becomes darker and finally stops changing, indicating reaction completion. An overnight reaction time is generally sufficient. The product is then collected and purified through dialysis or filtration. It is interesting to note that if the interfacial polymerization is performed with surfactants co-dissolved with aniline in the organic layer, then polyaniline forms only at the interface creating a free-standing film.[19]

UV/vis spectra of the purified nanofibers show that they are in the emeraldine oxidation state with peaks centered around 340, 440, and 800 nm.[3] The emeraldine oxidation state of polyaniline contains half imine and half amine nitrogens and can be represented by the formula [-C$_6$H$_4$−N═C$_6$H$_4$═N−C$_6$H$_4$−NH−C$_6$H$_4$−NH-]$_n$. The imine nitrogens can be completely protonated on exposure to strong acids, leading to doped polyaniline. Dedoped polyaniline is obtained by deprontonation on exposure to strong base.

The morphology of the products can be imaged using electron microscopy. Highly uniform nanofibers are observed in samples prepared from dispersions after dialysis under both transmission electron microscopy and scanning electron microscopy.[3] For the powders obtained after filtration, scanning electron microscopy images reveal that they are actually agglomerations of nanofibers

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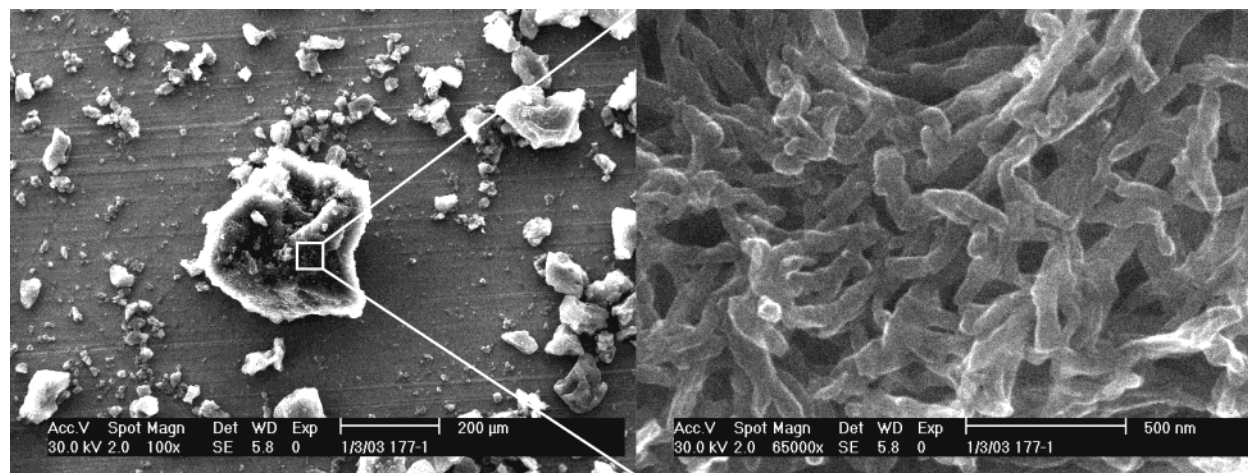
Figure 2. Polyaniline powders obtained after filtration. Scanning electron microscopy images show that the powders (left; low magnification, ×100) are agglomerations of nanofibers (right; high magnification, ×65 000).
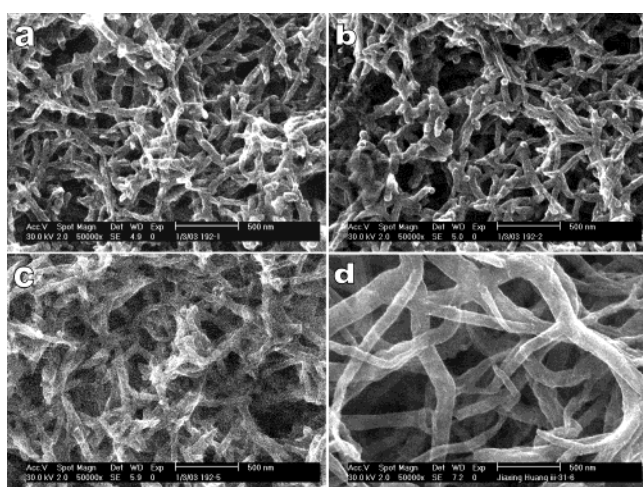

Figure 3. Scanning electron microscopy images of polyaniline nanofibers made by interfacial polymerization in a water/methylene chloride system, with the following acids in the aqueous phase: (a) HCl, (b) H$_2$SO$_4$, (c) HNO$_3$, and (d) HClO$_4$.

(Figure 2). The morphology of the nanofibers is unaffected when the dopants are removed with base.

Morphology. (a) Effects of Dopants. Nanofibers appear to form no matter what acid dopant is used in the polymerization. For example, very uniform nanofibers are observed in scanning electron microscopy images after interfacial syntheses using the mineral acids: hydrochloric, sulfuric, nitric, and perchloric acids (Figure 3a−d, respectively). Note that traditional chemical polymerization using common mineral acids yields granular polyaniline.[20,21] Nanofibers are also obtained when interfacial polymerization is carried out using many other acids, including phosphoric, acetic, formic, tartaric, methylsulfonic, ethylsulfonic, camphorsulfonic, or 4-toluenesulfonic acid. The diameters of the resulting nanofibers are affected by the dopants used in the polymerization as is apparent from the transmission electron microscopy images shown in Figure 4. The average diameter of nanofibers produced in HCl is about 30 nm (Figure 4a), those made in camphorsulfonic acid approach 50 nm (Figure 4b), and those synthesized in perchloric acid are centered around 120

nm thick (Figure 4c). Other acids, including sulfuric, nitric, and 4-toluenesulfonic acids, yield average diameters between 30 and 50 nm.

Camphorsulfonic acid (CSA) doped and dedoped nanofibers with average diameters around 50 nm are used as representative examples to investigate the surface area of the nanofibers, which could be important for applications such as sensors. The BET surface area of camphorsulfonic acid doped nanofibers is 41.2 m^2/g. After dedoping with base, the surface area increases from 41.2 to 49.3 m^2/g. This indicates that the free volume of the nanofiber sample increases after the dopants are removed, consistent with observations of conventional polyaniline.[22] On the other hand, the surface area of the nanofibers increases as the average diameter decreases: the measured value of HCl dedoped nanofibers (average diameter = 30 nm) is 54.6 m^2/g, which is greater than that of CSA dedoped nanofibers (average diameter = 50 nm, 49.3 m^2/g) or HClO$_4$ dedoped nanofibers (average diameter = 120 nm, 37.2 m^2/g).

(b) Effects of Synthetic Conditions. The synthesis of nanofibers appears to be insensitive to both the polymerization temperature and the monomer concentration. In the range between the freezing and boiling points of the solvents used in the syntheses (typically 5−60 °C), the nanofibers obtained look similar in both size and uniformity. However, when the reaction is carried out at −12 °C with 5 M LiCl in the water phase, most of the products are particle agglomerations. The monomer concentration in the organic phase can also be varied. For example, while keeping the aqueous phase unchanged, the relative volume of organic solvent can be decreased by increasing the concentration of aniline. When the aniline concentration is varied from 0.032 to 1.6 M, no significant effect is found on the observed morphology. This is potentially a great advantage for scaling up reactions since less organic solvent is needed.

The quality/uniformity of the nanofibers seems to be affected only by the acid concentration of the aqueous phase. The lower the concentration of acid, the lower the fraction of nanofibers observed in the final product. For example, when HCl is used as the dopant, higher concentrations (0.5−2 M) are preferred since larger yields of high-quality nanofibers are obtained (see Figure 3a and Figure 4a). As the concentration of HCl is

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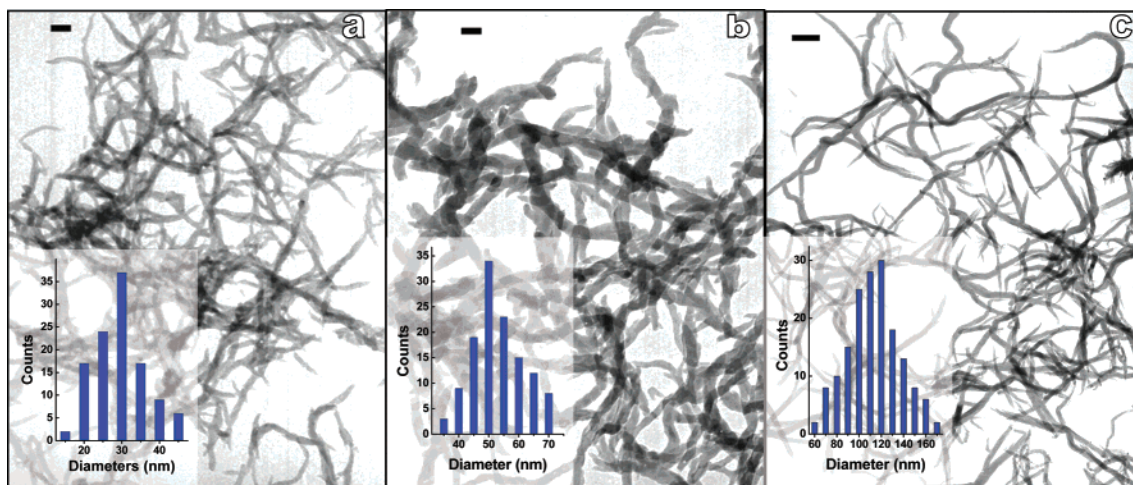(22) Anderson, M. R.; Mattes, B. R.; Reiss, H.; Kaner, R. B. *Science* **1991**, *252*, 1412−1415.

Figure 4. Transmission electron microscopy images of polyaniline nanofibers made by using (a) HCl (scale bar = 100 nm), (b) camphorsulfonic acid (scale bar = 100 nm), and (c) HClO₄ (scale bar = 1 μm). The insets show the diameter distributions (nm) of the doped nanofibers (scale bars = 500 nm).
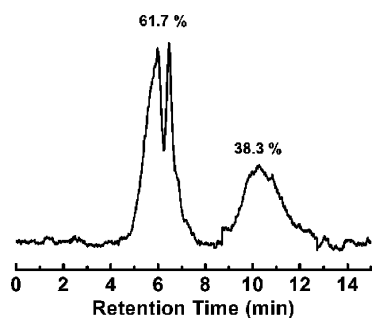

Figure 5. Gel permeation chromatogram of HCl dedoped polyaniline nanofibers. Based on polystyrene standards, the peaks (from left to right) correspond to molecular weights of 800 000, 550 000, and 24 000, respectively.

lowered, the quantity of granular particles starts to increase and finally prevails over the nanofibers. Similar results are obtained when the concentration of camphorsulfonic acid is varied. When medium or weak acids are used, such as tartaric acid (pK_a = 3.03) or pyrrolidone-5-carboxylic acid (pK_a = 3.32), even at high concentrations (1 M), the products are mixtures of particles and fibers. Therefore, high concentrations of strong acids are optimal for making polyaniline nanofibers. This is consistent with the traditional chemical polymerization, which uses ≥1.0 M HCl. Therefore, forming an aqueous/organic interface is the only major difference in our synthesis of nanofibers versus the classical method, which produces polyaniline particles.

The electrical conductivity of a pressed pellet of polyaniline nanofibers made with 1.0 M HCl is about 0.5 S/cm. This is comparable to conductivity reported for conventional polyaniline powders.[21]

The molecular weight distribution of the polyaniline nanofibers is determined using gel permeation chromatography (Figure 5). Although a bimodal distribution of molecular weights is observed, similar to that of conventional polyaniline,[23] the area under the high molecular weight peak (61.7%) is considerably larger than that under the low molecular weight peak (38.3%). This contrasts with conventional chemically polymerized polyaniline, for which the low molecular weight fraction dominates.[23] Since the chemical reaction used in the interfacial polymerization is the same as that used in the traditional synthesis, it is not

surprising that the molecular weight of nanofibers follows a similar bimodal distribution. However, compared to the traditional single-phase synthesis, there are fewer nucleation sites in an interfacial polymerization reaction. In the traditional homogeneous single-phase synthesis, the initiator molecules are mixed three-dimensionally with the monomer molecules in bulk solution. Therefore, each molecule of the initiator is capable of creating a nucleation center for polyaniline chain growth. However, in interfacial polymerization, the interaction between initiator molecules and monomers are limited to essentially a two-dimensional space—the aqueous/organic interface. Therefore, only those initiator molecules at the interface are capable of producing nucleation centers. This is likely the reason for the greater fraction of higher molecular weight components for interfacially polymerized polyaniline. Note that interfacial polymerization is known to produce relatively high molecular weight polymers for polyamides, polyesters, polyurethanes, and other conventional polymers.[24]

Dopant Induced Solubility. In most aqueous/organic systems, polyaniline is dispersed in the water phase since protonated polyaniline in the emeraldine salt form is hydrophilic. However, there are exceptions, for example, when the organic acid camphorsulfonic is used in the synthesis. Camphorsulfonic acid doped polyaniline nanofibers are found dispersed in the top water layer after reaction when carbon tetrachloride or carbon disulfide is used in the bottom organic layer (Figure 6a, inset). However, when chloroform or methylene chloride is used, polyaniline first diffuses into the aqueous phase, but then migrates into the bottom organic layer (Figure 6b inset). This can be explained by the well-known counterion induced solubility of polyaniline in organic solvents.[25] Polyaniline collected in the organic layer shows no nanoscale features (Figure 6b), which differs greatly from the nanofibers (Figure 6a) collected from the water layer.

Mechanism. The traditional oxidative chemical polymerization route is known to yield granular polyaniline, while interfacial polymerization produces nanofibers. By carefully examining the morphology of traditionally synthesized polyaniline powders,[1] we have found that there is also a small portion of nanofibers in addition to granular particle agglomerations

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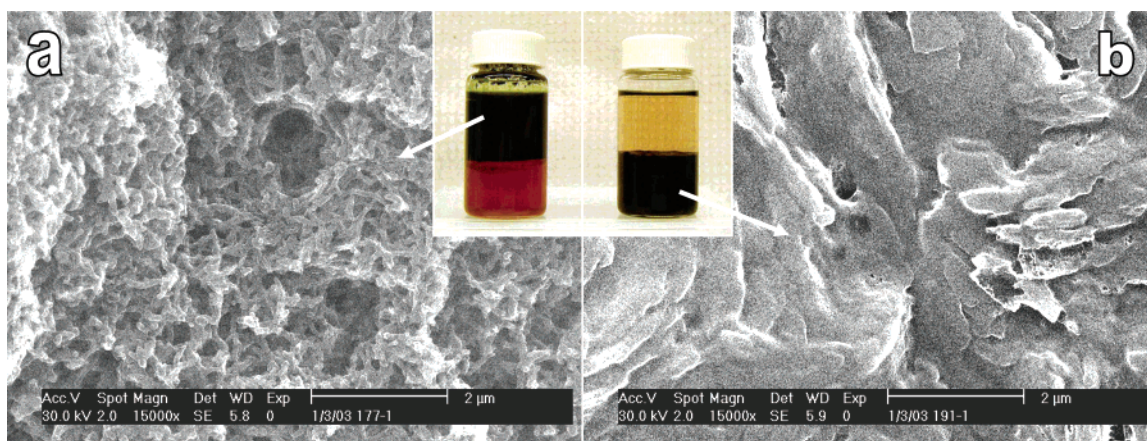(25) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1992**, *48*, 91−97.

Figure 6. Morphologies of polyaniline made by interfacial polymerization with camphorsulfonic acid in the aqueous phase when (a) CCl$_4$ and (b) CHCl$_3$ are chosen as the organic phase. The insets show the two reaction vials corresponding to a and b. Note that in both vials the less dense aqueous phase is on the top.
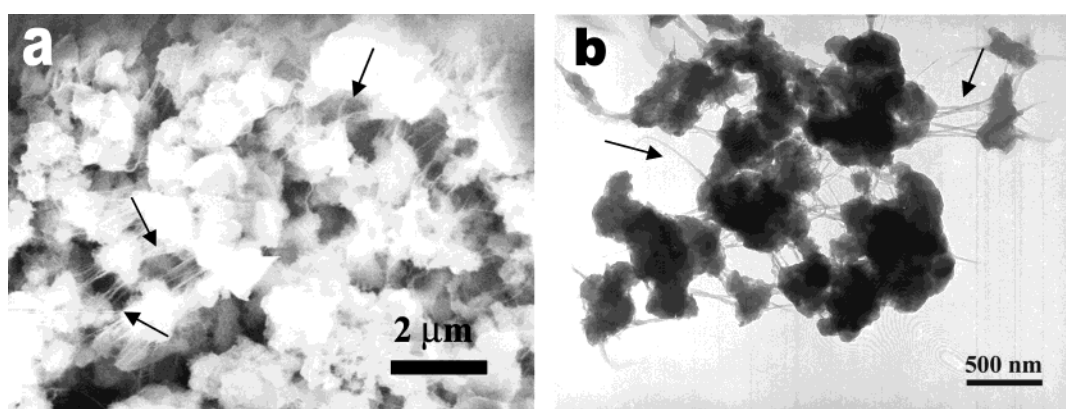

Figure 7. SEM (a) and TEM (b) images of polyaniline powders made by traditional chemical polymerization using 1.0 M HCl showing a small portion of nanofibers (arrows) in the sample.

(Figure 7a,b). These nanofibers appear very similar in size and shape to those obtained by interfacial polymerization. This indicates that the formation mechanism of polyaniline nanofibers is probably not related to the aqueous/organic interface, but rather associated with the oxidative chemical polymerization process itself and the linear nature of polyaniline chains. In interfacial polymerization, polyaniline forms at the interface (Figure 1b) and then migrates into the upper water layer (Figure 1d); even though its density is higher than water (∼1.3 g/cm^3).[26] Since the polymerization occurs only at the interface, once polyaniline leaves, the polymerization should terminate. Hence, the nanofibers are not subject to further polymerization producing almost exclusively nanofibers. Contrast this with conventional synthesis in which the freshly formed polyaniline is still surrounded by monomer and oxidant species. Even if nanofibers form initially as suggested by Figure 7, they will likely become the "nucleation" centers for further polyaniline precipitation and finally grow into irregularly shaped granular particles. Therefore, very few if any nanofibers are observed. If the nucleation step, i.e., the formation of the nanofibers and the secondary growth of polyaniline, can be separated, then the relative fraction of nanofibers and granular particles can be tuned. Interfacial polymerization may thus be an effective method to suppress secondary growth of polyaniline by removing the nanofibers from the reactive interface.

Conclusions

Interfacial polymerization is a general method to make bulk quantities of polyaniline nanofibers. The synthetic conditions are very flexible and can be performed with a broad selection of solvents, doping acids, monomer concentrations, and reaction temperatures. Although the choice of dopant acid is not critical to the synthesis of nanofibers, it does affect their diameters. The average diameter of nanofibers can be varied from 30 nm using hydrochloric acid to 120 nm using perchloric acid. This general synthetic method could make polyaniline nanofibers a materials platform for systematic studies of conducting polymer nanostructures. It should also stimulate the exploration of applications of these nanofibers especially in fields such as sensors, catalysis, and composite materials.

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