Synthesis of Polyaniline Nanofibers by "Nanofiber Seeding"

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We describe an extremely simple "nanofiber seeding" method to synthesize bulk quantities of nanofibers of the electronic polymer polyaniline in one step without the need for large organic dopants, surfactants, and/or large amounts of insoluble templates.[1] Seeding a conventional chemical oxidative polymerization of aniline with even very small amounts of biological, inorganic, or organic nanofibers (usually <1%) dramatically changes the morphology of the resulting doped polyaniline powder from nonfibrillar (particulate) to almost exclusively nanofibers. These findings could have widespread applications in morphological control in all precipitation polymerization reactions.

Conventional chemical oxidative polymerization approaches to nanostructured electronic polymers include the use of insoluble solid templates such as zeolites,[2] opals,[3] and controlled pore-size membranes,[4] or soluble templates such as polymers[5] and surfactants.[6] A "nontemplate" approach has also been described in which the use of large organic anions results in polyaniline nanofibers and nanotubes having average diameters in the 650−80 nm range.[7] Recently, an interfacial polymerization method has been reported where ∼50 nm diameter fibers of polyaniline are produced at the interface of two immiscible liquids.[8] We believe that, despite the diversity in these synthetic approaches, the dramatic change in polymer morphology points to an underlying mechanistic rationale; that is, polymeric nanostructures formed (or present) during the very early stages of the reaction can orchestrate bulk formation of similar nanostructures. This paper describes evidence consistent with the above rationale where seeding the reaction with very small amounts of nanofibers, regardless of their chemical nature, results in a precipitate with bulk fibrillar morphology.

Seed nanofibers were chosen from a variety of organic, inorganic, and biological systems: (a) ∼50 nm diameter polyaniline nanofibers,[8] (b) ∼20 nm diameter single-walled carbon nanotube bundles (SWNT) made by the HiPco route,[9] (c) ∼12 nm diameter nanofibrous hexapeptide, AcPHF6 (Ac-VQIVYK-amide), itself a seed in the polymerization of Alzheimer's disease tau protein,[10] and (d) ∼15 nm diameter nanofibers of V_2O_5.[11]

The experimental details of the synthesis are described elsewhere.[12] The SEM images of the polyaniline powder obtained in all seeded experiments show fibrillar morphology with fibers having an average diameter in the range 20−60 nm (Figure 1). It is important to note that just 1−4 mg of the seed nanofibers was sufficient to change the morphology of the bulk precipitate (∼200 mg) quantitatively to nanofibers (also confirmed by TEM). Unseeded reactions (conventional synthesis) or reactions seeded with particulate polyaniline powder yielded emeraldine·HCl precipitate having nonfibrous, particulate morphology.[12] When the reaction is seeded with nanospheres of polypyrrole·Cl (∼50 nm diameter), however, the emeraldine·HCl precipitate was also largely in the form of nanospheres (∼170 nm diameter).[12] Although the general shape of the seed appears to control the overall morphology of the precipitate (fibers vs particles), specific differences in the length, diameter, etc., of the seeds do not appear to have a significant impact.
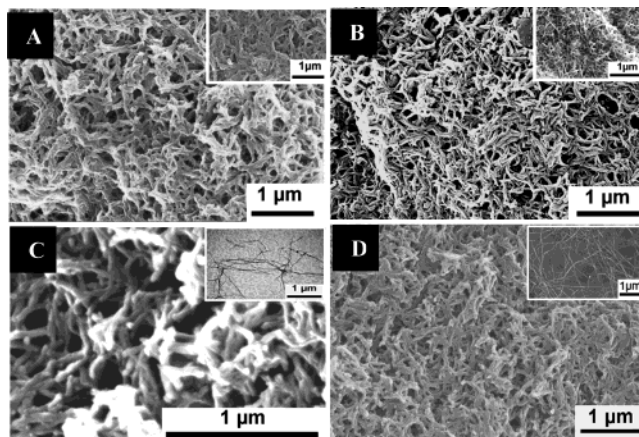

Figure 1. SEM images of emeraldine·HCl nanofibers synthesized by seeding the reaction using the following: (A) 1.5 mg of emeraldine·HCl nanofibers (SEM image inset), (B) 1.6 mg of HiPco SWNT (SEM image inset), (C) 1.0 mg of the hexapeptide AcPHF6 (TEM image inset), and (D) 4 mg of V_2O_5 nanofibers (SEM image inset). See also Supporting Information.

During the synthesis, the walls of the reaction flask were also coated with a dark-green film of in-situ deposited emeraldine·HCl. This film, normally observed during conventional chemical oxidative polymerization of aniline, has been extensively investigated in the past.[13,14] In SWNT seeded systems, this in-situ deposited film also has a nanofibrillar morphology (Figure 2A). These in-situ deposited films are thin (<1 μm), transparent, and strongly adherent, which permits their facile and rapid characterization without requiring cumbersome postsynthesis processing steps, for example, product isolation, spin coating, etc. This approach could be important in a variety of technological applications requiring the use of substrate-supported film, for example, sensors, displays, etc.

Spectroscopically, both powders and films of polyaniline nanofibers were essentially identical to conventional nonfibrillar emeraldine·HCl.[15] For example, the FT/IR (KBr pellet) and solution UV/vis (in NMP) spectra of the corresponding base forms are consistent with the polymer being in the emeraldine oxidation state,[16] and the UV/vis spectra of in-situ deposited films of the emeraldine·HCl and emeraldine base nanofibers on glass microscope slides (Figure 2B) are also similar to those obtained previously.[14] Four-probe pressed-pellet conductivities for polyaniline nanofibers were in the range 2−10 S/cm, similar to conventional emeraldine·HCl powder. There is also no significant difference in their aqueous electrochemistry; that is, the cyclic voltammogram of emeraldine·HCl nanofibers displays the two redox peaks characteristic of parent polyaniline[17] (inset, Figure 3).

There is, however, a significant difference in the capacitance values for polyaniline nanofibers. For example, a capacitance value of 122 F/g was obtained for emeraldine·HCl nanofibers synthesized using polyaniline (nanofibers) as the seed template as compared to 33 F/g in nonfibrillar emeraldine·HCl (Figure 3). Elevated capaci-
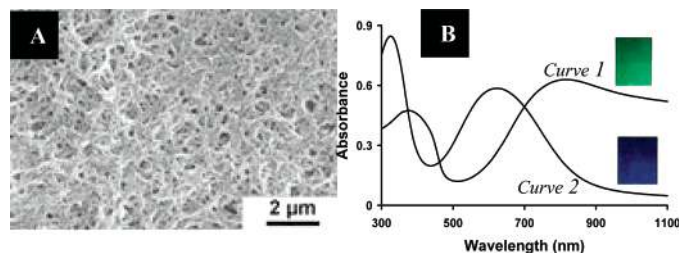
Figure 2. (A) SEM image (left) of an in-situ deposited film of emeraldine·HCl nanofibers on a glass microscope slide synthesized using 1.6 mg of SWNT seed template. (B) Solid-state UV/vis spectra and optical images of films of emeraldine·HCl (green, curve 1) and emeraldine base (blue, curve 2) on a glass microscope slide. See also Supporting Information.
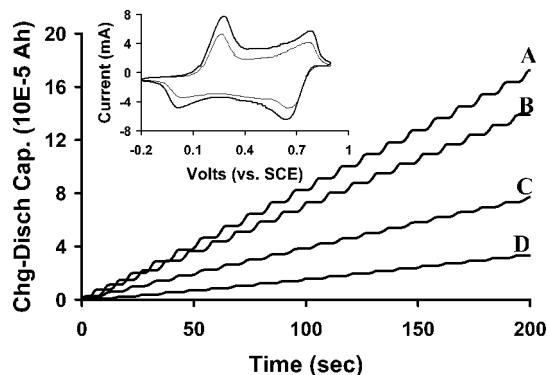

Figure 3. Charge/discharge capacity plot of emeraldine·HCl powder in the range 0.4−0.5 V (vs SCE) in aqueous 1.0 M camphorsulfonic acid electrolyte. Charge (curve A), discharge (curve B) cycles for nanofibers and charge (curve C), discharge (curve D) cycles for conventional (nonfibrillar) polyaniline. Inset: cyclic voltammograms of polyaniline nanofibers (outer plot) and conventional polyaniline (inner plot).

tance values were obtained for all seeded systems. The voltage range 0.4−0.5 V (vs SCE) was chosen because it falls in the valley between the two redox peaks of polyaniline (see inset in Figure 3). The charge/discharge cycles are also more symmetrical in a nanofiber (Figure 3, curves A, B), which is consistent with their increased available surface area that is expected to improve the kinetics of the various processes involved. We believe this could play an important role in the development of next-generation energy storage devices.

The reasons for the fibrillar morphology in all seeded systems are not clear, although we believe it could be related to fibrillar morphology observed in the electrochemical polymerization of aniline in the presence of the aniline dimer, *N*-phenyl-1,4-phenylenediamine.[18] Two important factors common to this class of precipitation polymerization reactions are as follows: (i) there is an induction period followed by a rather rapid formation of a precipitate, and (ii) the influence of inert surfaces (walls of the reaction flask, etc.) on progress of the reaction. We believe that polymerization first occurs on the surface of the seed template whose morphology is mirrored by the growing polymer chain. Indeed, a blue-green film of pernigraniline salt is formed on the walls of the reaction flask, magnetic stir bar, etc., well before any precipitate is observed in bulk.[13] This in-situ deposited film of (fibrillar) pernigraniline salt can then seed fresh polymer growth triggering a continuous seeding process resulting in a bulk precipitate in which the nanoscale morphology of the original seed template is transcribed over many length scales. This phenomenon can also be extended to other electronic polymers, for example, polypyrrole and PEDOT.

The effect that even small amounts of insoluble substances can have on the properties of the final product is surprising and raises important questions and concerns in the area of precipitation polymerization in general and synthesis of electronic polymers in particular. For example, we believe that, during the chemical or electrochemical synthesis of electronic polymers, special care must taken to ensure that the reaction system is free of particulate matter like inadventitious dust, fabric lint, etc. It is perhaps not surprising that one can find in the literature several examples of polyaniline synthesized using "established procedure" but exhibiting very different properties, raising questions that have been consistently voiced by the scientific community.[19]

In summary, we demonstrate the development of emergent nanostructures in electronic polymers over multiple length scales triggered by very small amounts of added nanoscale templates. Described for the first time are the following: (i) the use of nanostructured seed templates to synthesize rapidly, and in one step, bulk quantities of doped polyaniline nanofibers without the need for conventional templates, surfactants, polymers, or organic solvents, (ii) a convenient method to obtain thin, substrate-supported, transparent films of nanofibers of polyaniline without requiring any bulk processing steps, (iii) increased capacitance values in polyaniline nanofibers synthesized by the nanofiber seeding method, and (iv) a general phenomenon impacting the field of precipitation polymerizations that could facilitate the design of next-generation electronic polymer systems requiring nanometer scale control of surface architecture.

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

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