

Synthesis of Extra-long Polyaniline Nanofibers

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Abstract

One-dimensional (1-D) nanostructures of polyaniline are known to be important in various applications such as chemical sensors, actuators, organic memories, and photovoltaic devices. Compare to other synthetic routes to polyaniline nanofibers, the method our lab developed, the rapidly mixed method, has the advantage of producing highly uniform nanofibers with diameters less than 100nm through a simple reaction, while the disadvantage is that such nanofibers are relatively short. In our study, extra-long nanofibers of polyaniline have been synthesized through the incorporation of various aromatic additives such as benzenediamine, aniline dimer, and aniline tetramer on a catalytic scale. Such additives play the role of initiators in the reaction and serve as homogeneous nucleation sites for the growth of polymer chains, which results in the formations of extra-long nanofibers. For example, the polyaniline polymerization initiated by aniline tetramer produces nanofibers with an average length of roughly 30 μ m and approximately 100nm in diameter. In contrast, nanofibers synthesized through conventional methods are only a few micrometers in length with similar diameters. Further measurement and characterization will be conducted

Background

Existing synthetic methods for PANI nanofibers: templates, surfactants, inorganic seeds, electrospinning, etc

Disadvantages: not inherently pure, not scalable, complicated procedures

Synthetic method developed by our lab: rapidly mixed reactions with no stirring – mix the oxidant solution and monomer solution rapidly

Initiators: aromatic additives that serve as homogeneous nucleation sites – greatly enhance reaction rate \rightarrow favor nanofiber formation

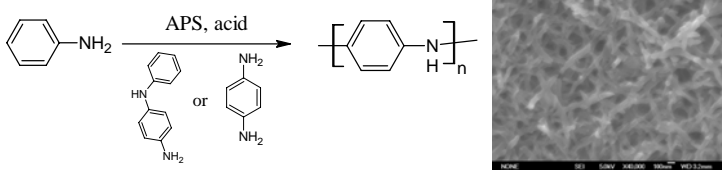


Figure 1. Chemical equation of the polyaniline polymerization reaction with initiators and the resulting SEM image of such reactions.

Advantages of our method: pure, simple, scalable, inexpensive

Disadvantages of our method: fibers are relatively short and highly entangled

Challenge

Produce long and less entangled PANI nanofibers while maintain the purity, simplicity, and scalability of our synthetic method

Approach 1: modify synthetic conditions

Factors	Conditions	Actions	New conditions
[initiator]	1mM	No change	1mM
[aniline]	0.32M	Dilute	0.08M
[oxidant]-to-[aniline] ratio	1:4	Decrease	1:18
Solvent	H ₂ O	No change	H ₂ O
Dopant acid	HCl	Try different acids	HCl

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Explanations

No changes in [initiator]: avoid self coupling

Decrease [aniline]: less collisions between aniline molecules

Decrease [oxidant]-to-[aniline] ratio: less aniline molecules get oxidized

Same solvent and dopant acid: H₂O and HCl are well established as best solvent and dopant acid for such reactions

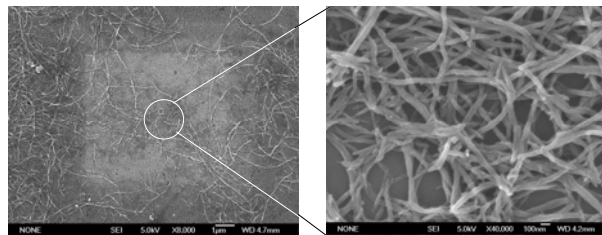


Figure 2. New reaction conditions significantly promote PANI nanofiber growth. Such nanofibers have length ranges from 8 μ m - 12 μ m and diameters of roughly 40nm, which is identical to the typical PANI nanofibers.

Molecular Weight Studies

Polyaniline	M _n (Da)	M _w (Da)	PDI
Extra-long nanofibers	5300D	8100	1.5
Typical nanofibers	9100	25800	2.5 - 3.5
Agglomerates	N/A	N/A	5 - 6

The extra-long nanofibers of polyaniline has a significantly lower PDI, indicating the polymer chains are much more uniform than typical polyaniline nanofibers or agglomerates. The uniformity of the polymer chains might have contributed to its thin fibrous morphology.

Approach 2: higher aniline oligomer as initiator

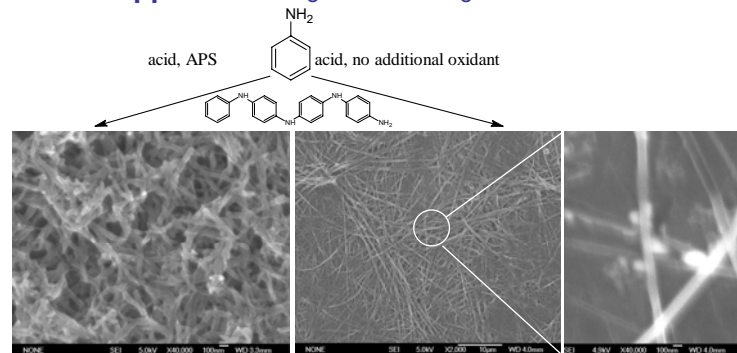


Figure 3. With APS, the polyaniline nanofibers produced exhibit typical length. However, by simply dissolving the aniline tetramer initiator in the monomer solution without additional oxidant, extra-long polyaniline nanofibers with average length of approximately 30 μ m and diameter less than 100nm were obtained.

Conclusions

Being able to synthesize extra-long nanofibers through our rapidly mixed method helped to overcome its biggest disadvantage and made this method the most competitive candidate for commercializing polyaniline nanofibrous mats. Also, thin films made out of such extra-long nanofibers of polyaniline are expected to possess higher conductivity than typical nanofibers, which will enhance their performances in various electronic devices.