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Frank D. Blum

Missouri University of Science and Technology

Sunil K. Pillalamarri

Lalani K. Werake

J. Greg Story

Missouri University of Science and Technology, story@mst.edu

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/chem_facwork/2661

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NANOMETAL CONTAINING NANOCOMPOSITES AND PHOTOLITHOGRAPHIC POLYANILINE NANOFIBERS

Frank D. Blum,^a Sunil K. Pillalamarri,^a Lalani K. Werake,^b J. Greg. Story,^b Massimo F. Bertino^b and Akira T. Tokuhira^c

^a Department of Chemistry; ^b Department of Physics

^c Department of Nuclear Engineering

University of Missouri-Rolla, Rolla, MO 65409

Introduction

There is considerable interest in the use of nanofibers and nanoparticles in electronic devices. These materials have potential application in sensors, actuators, and memory, to name just a few.^{i,ii} The size of the materials used may improve sensitivity because of their high specific surface areas. The nanoparticles may also have properties that are inherently different from their bulk counterparts. The use of synthetic polymers may result in considerable mass savings over conventional metal-based systems. It is clear that these systems have many potential advantages, however, there is still a great deal to be learned about how to make and characterize them.

In our laboratories, we have recently shown that it is possible to make a variety of nanostructures based on polyaniline and polypyrrole with a variety of different techniques. In the present report, we review some of our work with a focus on nanofibers, one-pot synthesis of metal nanoparticle nanocomposites, and the patterning of conductive nanofibers. We believe that these systems will be useful in novel or significantly improved devices.

Experimental

The syntheses of the materials discussed have been described in some detail in other publications. Consequently, only brief outlines will be given here. For the synthesis of polyaniline nanofibers,ⁱⁱⁱ differing amounts of aniline, an oxidizer (such as benzoyl peroxide, BPO, or ammonium persulfate, APS), a dopant (usually a strong mineral acid), and water were mixed to form solutions. These solutions were irradiated in vials in UMRs nuclear reactor about an hour after reactor shutdown. The dose rates varied from about 1.5 to 0.3 kGy/h over the irradiation period (up to 24 h). The nanofibers were centrifuged, filtered, washed with water, and then dried. We note that in these systems, no additional templates or capping agents were required.

Nanofibers decorated with metal nanoparticles were formed with the addition of metal ions to solutions similar to those used to prepare nanofibers. A variety of different metal salts could be used as starting materials. For example, for silver, AgNO₃ and for gold, HAuCl₄ were used.^{iv,v} In the latter case, the residuals from the hydrogen tetrachloroaurate compound also served as the dopant. The composites were made in one pot. The particles were stuck to the nanofibers and were removed, only with difficulty, by sonication.

Solutions of polyaniline were also patterned using UV light.^{vi} Thin films of the aniline solutions mentioned above were spin-coated on silica wafers and then exposed to UV radiation for various amounts of time.

Results and Discussion

There are several advantages to preparing polyaniline nanofibers via the routes described above and in previous work.ⁱⁱⁱ An example of the structures formed are shown in Figure 1. These fibers were formed from a 0.1 M aniline, 0.002 M ammonium persulfate, and 0.3 M HCl. This sample was irradiated with γ -rays. Fibers made by this technique had diameters from 50 to 100 nm and were as long as a few μ m. When much greater amounts of the oxidizer were used, larger "rods" of polyaniline were produced with diameters measuring as much as 250 μ m.

An example of nanofibers that are decorated with gold nanoparticles^{iv} is shown in Figure 2. These materials were also made in a single pot, but the apparent mechanism was more complicated than that of either conducting nanofibers or metal nanoparticles themselves. We observed that the reaction appears to take place with the initial formation of oligo- and polyaniline. The radiolysis process resulted in a number of active species in solution. Most prominent of which were solvated electrons. These have the potential to reduce metals, which may form nanoparticles if an appropriate "capping agent" is present.^{vii} However, in our polyaniline/metal ion systems, an

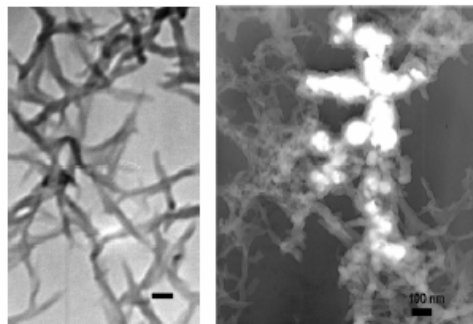


Figure 1. TEM of polyaniline nanofibers. The scale bar represents 200 nm.ⁱⁱⁱ

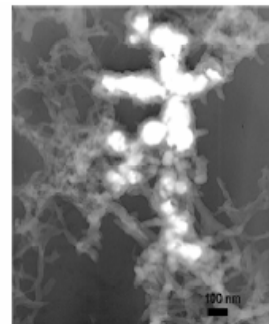


Figure 2. TEM of nanogold particles (bright) decorating polyaniline fibers (medium brightness).^v

oxidizer like ammonium persulfate is also used. In the initial stages of the reaction, the oxidizer activated the aniline and aniline oligomerization/polymerization occurred. During this time, we believe that the presence of the oxidizer retarded metal formation, possibly by re-oxidizing the metals reduced by solvated electrons. The formation of the metal particles did not occur until the oxidizer was used up. We also believe that the aniline, oligoaniline and polyaniline acted as templates or capping agent for both the polymer and metal nanoparticles.

The ability for the lithographic patterning of polyaniline with UV radiation is shown in Figure 3. The dark stripe is the irradiated portion and consists of nanofibers similar to those produced with γ -irradiation. The light areas also polymerize, but to a bulk-like morphology since they were not irradiated. This contrast between the nanostructures of the materials should lead to new devices based on them.

Conclusions

We have demonstrated that novel structures of nanofibers can be made with relatively simple synthesis techniques. These nanofibers can be made without the addition of a separate template, and with the addition of the proper metal ions, they can be decorated with metal nanoparticles. They can be made not only with high-energy radiation, but also with UV radiation, which was shown to allow patterning of the materials. We believe that these materials have significant potential for novel electronic devices.

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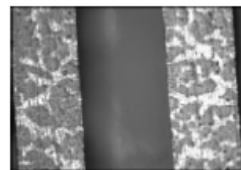


Figure 3. Photolithographed polyaniline. The middle (dark region) was irradiated with UV light and is 200 μ m wide.^{vi}

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