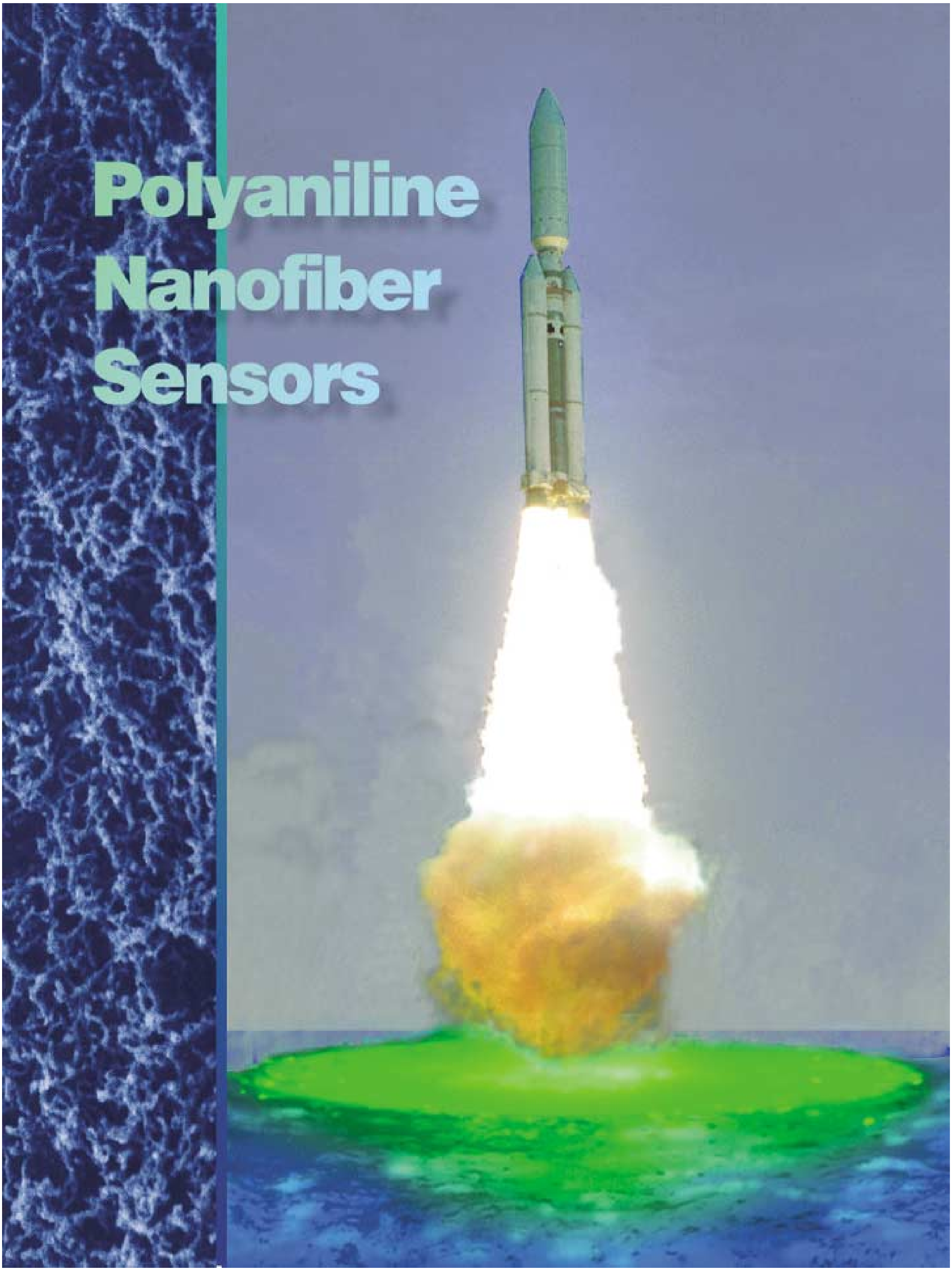

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Nanostructured Polyaniline Sensors

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Abstract: The conjugated polymer polyaniline is a promising material for sensors, since its conductivity is highly sensitive to chemical vapors. Nanofibers of polyaniline are found to have superior performance relative to conventional materials due to their much greater exposed surface area. A template-free chemical synthesis is described that produces uniform polyaniline nanofibers with diameters below 100 nm. The interfacial polymerization can be readily scaled to make gram quantities. Resistive-type sensors made from undoped or doped polyaniline nanofibers outperform conventional polyaniline on exposure to acid or base vapors, respectively. The nanofibers show essentially no thickness dependence to their sensitivity.

Keywords: interfaces · nanostructures · polyaniline · sensors · thin films

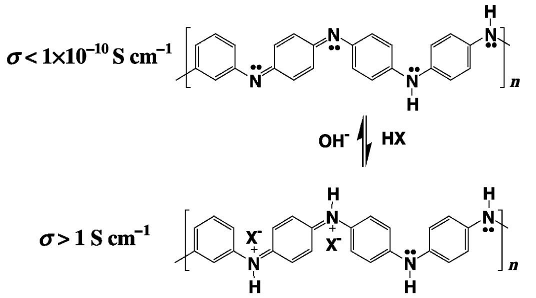

Figure 1. Repeat unit of the emeraldine oxidation state of polyaniline in the undoped, base form (top) and the fully doped, acid form (bottom). Doping can be carried out with any strong acid, HX, where X serves as the counterion to maintain charge balance. Dedoping can be accomplished with any strong base, OH^-.

Introduction

Since the discovery that conjugated polymers can be made to conduct electricity through doping,[1] a tremendous amount of research has been carried out in the field of conducting polymers.[2] Polyaniline is a unique conjugated polymer in that it can be tailored for specific applications through a non-redox acid/base doping process.[3] The electrically conductive form of polyaniline is known as the "emeraldine" oxidation state (Figure 1), which, when doped with an acid, protonates the imine nitrogens on the polymer backbone and induces charge carriers.[3] The conductivity of polyaniline increases with doping from the undoped insulating emeraldine base form ($\sigma < 10^{-10}\,\mathrm{S\,cm^{-1}}$) to the fully doped, conducting emeraldine salt form ($\sigma > 1\,\mathrm{S\,cm^{-1}}$).[3] Dopants can be added in any desired quantity until all imine nitrogens (half of the total nitrogens) are doped, simply by controlling the pH of the dopant acid solution. Dopants can be removed by the interaction of the emeraldine salt form with common bases such as ammonium hydroxide.

Since the conductivity of polyaniline depends on both its ability to transport charge carriers along the polymer backbone and for the carriers to hop between polymer chains,[4] any interaction with polyaniline that alters either of these processes will affect its conductivity. This is the underlying chemical principle enabling polyaniline to be used as the selective layer in a chemical-vapor sensor, such as resistance-type detectors known as chemiresistors. Due to their room temperature sensitivity, the ease of deposition on to a wide variety of substrates and the rich chemistry of structural modifications, polyaniline[5–7] as well as other conducting polymers[8–11] are becoming attractive materials for sensor applications.

A polyaniline chemiresistor typically consists of a substrate, electrodes, and the polymer selective layer (Figure 2). Changes in conductivity of the polymer film upon exposure

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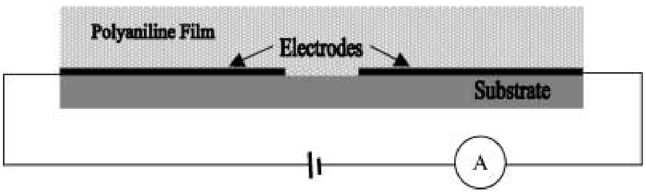

Figure 2. A schematic diagram of a polyaniline chemiresistor consisting of a polyaniline film, electrodes, substrate and the electronic components needed to monitor current flowing through the resistor.

to vapors can be readily monitored with an ohmmeter or electrometer. A great deal of polyaniline sensor research has focused on changing the polymer structure to facilitate interaction between vapor molecules and polymer either by modifying the polymer backbone or the interchain connections.[5,7] However, poor diffusion can readily outweigh any improvements made to the polymer chains, since most of the material, other than the limited number of surface sites, is not available for interacting with the vapor, thus degrading sensitivity (Figure 3).[12] One way to enhance diffusion is to reduce film thickness, such as producing monolayers of conventional material;[13,14] this leads to a trade-off between sensitivity and robustness. Coating polyaniline on porous supports can increase the surface area and has been widely reported,[15–20] but the extra chemistry and physics involving polymer/support and polymer/support/electrode interfaces needs to be considered.

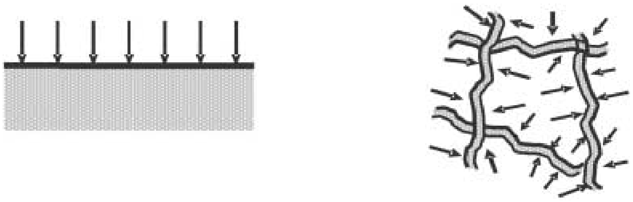

Figure 3. Schematic diagram of a conducting polymer thin film (left) and nanofibers (right) exposed to gas molecules (arrows). Compared to a thin film, nanofibers have a much higher fraction of exposed surface (black), and much shorter penetration depth (gray) for gas molecules.

The use of nanostructured polyaniline, such as nanowires, nanotubes, nanofibers, or nanorods, could greatly improve diffusion, since nanostructured polyanilines have much greater exposed surface area, as well as much greater penetration depth for gas molecules (see Figure 3), relative to their bulk counterparts. For example, the surface area per unit mass (S_A) of polyaniline nanofibers increases geometrically as the diameters (d) of the nanofibers decrease ($S_A \sim 1/d$). Even when the thickness of an ultra-thin film is the same as the diameters of the nanofibers, the fibers should still outperform a thin film, since they have higher surface-to-volume ratios due to their cylindrical morphology.[21] The small diameter of the nanofibers (<100 nm) coupled with the possibility of gas approaching from all sides should give sensors with improved performance. However, few reports exist on nanostructured conducting polymer sensors,[22,23] probably due to the lack of facile and reliable methods for making high quality conducting polymer nanostructures.

Synthesis of Polyaniline Nanostructures

The classical chemical synthesis of polyaniline uses aniline, an oxidant, and a strong mineral acid as a dopant.[3] Current chemical methods of making polyaniline nanostructures (tubes/fibers/wires/rods) usually require specific structure-directing materials added into the polymerization bath. The formation of polyaniline nanostructures relies either on the guidance of templates, for example, channels of zeolites[24] or nanoporous membranes,[25] or the self-assembly of functional molecules such as surfactants,[26] polyelectrolytes,[27] or complex organic dopants.[28] Therefore, the synthetic conditions have to be carefully designed to accommodate their use, and to remove them after synthesis to obtain pure polyaniline nanostructures. Electrochemical polymerization[29] and some physical methods, such as electro-spinning[30] and mechanical stretching,[31] can produce conducting polymer nanofibers without templates, but these materials have only been made on a very limited scale. Earlier work on the electrochemical synthesis of polyaniline indicated that some nanofibers form naturally on the surface, while the underlayer is much more compact.[3] For a systematic investigation into sensor properties, there is a need for a practical bulk synthetic method capable of making pure, uniform, and template-free polymer nanostructures with small diameters (<100 nm), on which chemical and/or physical modifications can be easily performed.

Recently, we have successfully developed a chemical synthesis to make polyaniline nanofibers in bulk quantities.[23] The synthesis is based on the classical chemical oxidative polymerization of aniline. Instead of using the traditional homogeneous aqueous solution of aniline, acid, and oxidant,[3] the polymerization is performed in an immiscible organic/aqueous biphasic system (Figure 4). Aniline polymerizes at the interface between an organic layer that contains dissolved aniline and an aqueous layer containing the oxi-

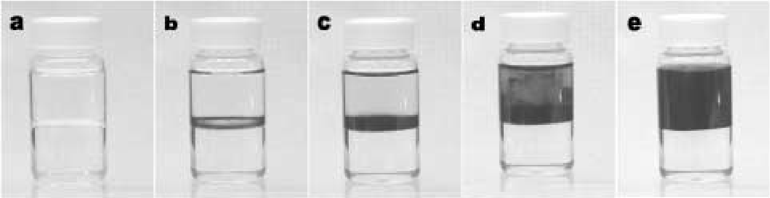

Figure 4. Snapshots showing the interfacial polymerization of aniline. The reaction times are a) 0, b) 60, c) 90, d) 120, and e) 180 seconds. The top layer is an aqueous solution of acid and oxidant, the bottom layer is aniline dissolved in an organic solvent.

dant and dopant. As the reaction proceeds, polyaniline forms across the interface, slowly diffusing into the water layer and eventually filling it. At the same time, the color of the organic layer turns red-orange due to the formation of byproducts, probably aniline oligomers. Allowing the reaction to proceed overnight gives it sufficient time to reach completion. The product is then collected and purified by either dialysis or filtration, yielding a product in the form of a water dispersion or a powder, respectively. Further washing or dialyzing with water yields pure, doped polyaniline that can be dedoped by washing or dialyzing with ammonia (Figure 5).

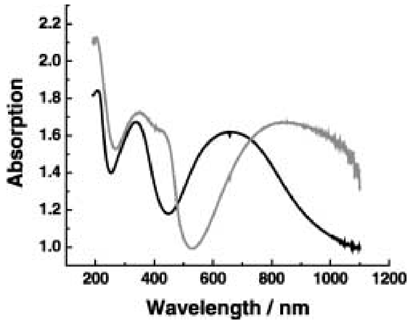

Figure 5. UV-visible spectra of HCl doped (gray) and dedoped (black) polyaniline nanofibers.

The products are polyaniline nanofibers with average diameters around 50 nm and lengths varying from 500 nm to several microns (Figure 6). High-quality polyaniline nanofibers with dopants ranging from mineral acids to organic acids can be made. The synthesis is readily scalable and can be carried out at room temperature. Gram-scale products containing almost exclusively nanofibers for sensor applications have been synthesized.

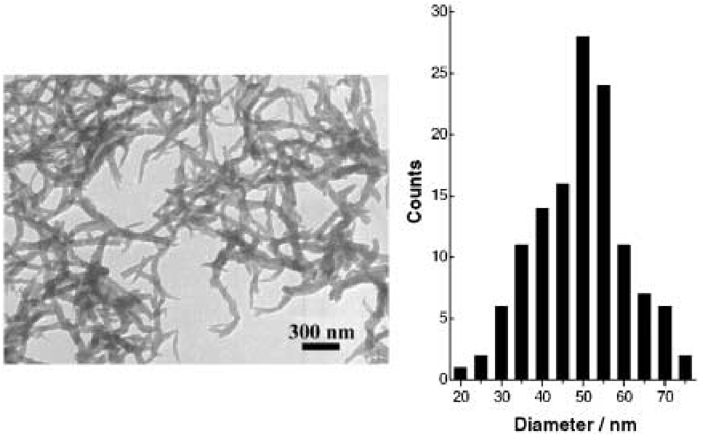

Figure 6. A typical transmission electron microscopy image of polyaniline nanofibers made by interfacial polymerization (left) and the corresponding size distribution (right).

Polyaniline Nanofiber Sensors

Thin films of conventional polyaniline and polyaniline nanofibers are coated on to interdigitated electrodes to compare their performance (Figure 7). Conventional polyaniline thin films are cast from an organic solvent, such as *N*-methylpyrrolidone or hexafluoroisopropanol. Polyaniline nanofiber thin films are cast from water suspensions obtained after dialysis. The electrode arrays, consisting of 23 pairs of interdigitated gold electrodes (0.18 μm thick) with gaps of either 10 or 40 μm, are fabricated on an insulating glass substrate. The real-time resistance changes of the dedoped films are monitored with an electrometer (Keithley 617), upon exposure to vapor.

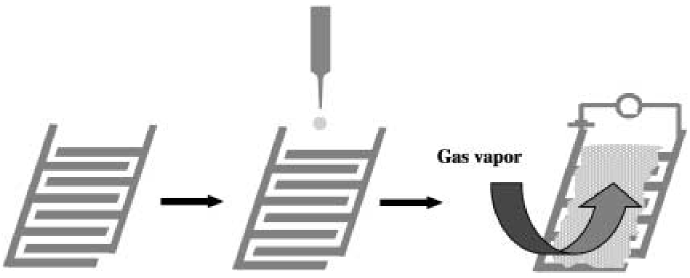

Figure 7. Schematic diagram showing a typical sensor experiment: gold interdigitated electrodes (left) are coated with a polyaniline film by drop-casting (middle), and the resistance of the film is monitored as the sensor is exposed to vapor (right).

The response given by conventional polyaniline and polyaniline nanofibers, both in the undoped emeraldine base form, upon exposure to 100 ppm of hydrochloric acid vapor are compared in Figure 8. Since HCl vapor is highly acidic, it dopes polyaniline and increases its electrical conductivity. The nanofiber film (~2.5 μm thick) gives a much greater response to HCl than a conventional polyaniline film (~1 μm thick), even though it is considerably thicker. This is probably due to the higher surface area of the nanofiber film; this allows more interaction between vapor molecules and the polyaniline. The BET surface area of polyaniline nanofibers of 50 nm in diameter is 49.3 $m^2 g^{-1}$, while that of conventional films is limited to the area of the film surface.[32]

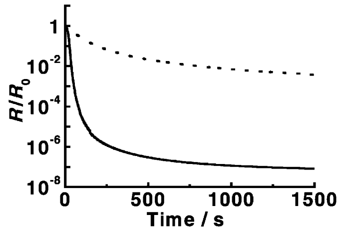

Figure 8. Resistance changes of a nanofiber emeraldine-base thin film (solid line) and conventional film (dotted line) upon exposure to 100 ppm HCl vapor in nitrogen. The resistance (R) is normalized to the initial value (R_0) prior to gas exposure.

The time response and corresponding sensitivity of polyaniline films to vapors are strongly thickness dependent (Figure 9). Generally thinner films result in better performance. As the thickness is decreased from 1 μm to 0.3 μm, the response time increases significantly and the magnitude of

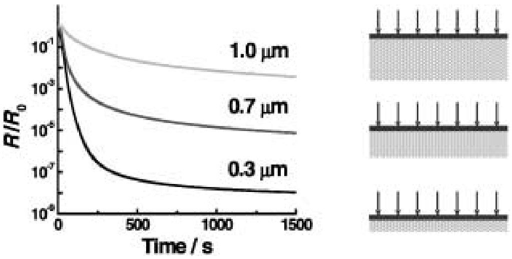

Figure 9. Resistance changes of conventional polyaniline films with different thicknesses upon exposure to 100 ppm of HCl vapor (left). The schematic diagram (right) shows the active polyaniline layer (black) interacting with vapor molecules (arrows) and the inactive supporting layer (gray).

the response at a fixed time increases by more than five orders of magnitude (Figure 9). Since only the outermost surface interacts with the vapor molecules, a thicker film has more inactive material that does not contribute to the sensing process at short times. Therefore, the performance of conventional polyaniline thin film sensors are limited by the thickness of the underlying polyaniline film.[23]

When nanofibers are used as the selective layer, the performance is essentially unaffected by thickness, at least in the range of 0.2–2 µm (Figure 10). This is probably due to the porous nature of nanofiber films, which allows vapor molecules to penetrate through the entire film and interact with all the fibers. Therefore, even in thicker films, all the fibers are able to contribute to the sensing process. The porous nature of the nanofiber films can be observed directly by using scanning electron microscopy (SEM, Figure 11). Here an SEM image of a nanofiber film on interdigitated electrodes used in sensor experiments is presented. The overview shows a uniform distribution of nanofibers. The cross-sectional view (inset) clearly shows that the film is porous. The thickness independence of sensitivity for nanofiber films eliminates the need to make very thin films to obtain good sensitivity.

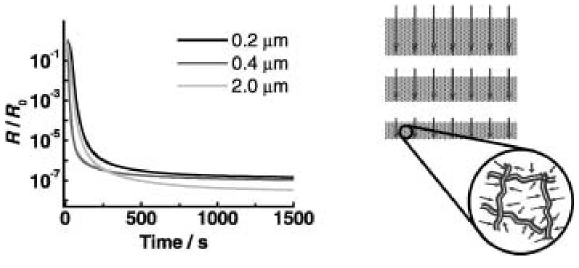

Figure 10. Response of polyaniline nanofiber sensors of different thicknesses upon exposure to 100 ppm of HCl vapor (left). The schematic diagram (right) illustrates that the vapor molecules (arrows) can interact rapidly with most of the polyaniline nanofibers (gray), since the films are porous.

Hydrochloric-acid-doped polyaniline films can be used as base sensors. When fully HCl-doped polyaniline is exposed to ammonia vapor, a drop in conductivity is observed. As expected, a nanofiber film outperforms a conventional polyaniline film (Figure 12). The nanofiber films again have essentially no thickness dependence, while the sensitivity of conventional polyaniline films is completely dependent on thickness.

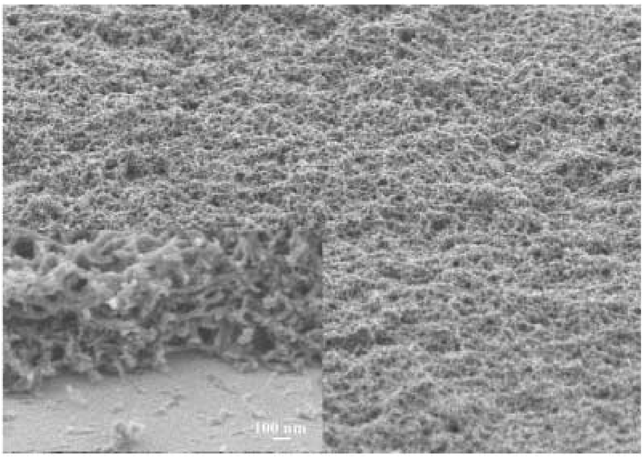

Figure 11. Scanning electron microscopy image showing an overview and cross-section (bottom left, inset) of a nanofiber film deposited on a glass substrate.

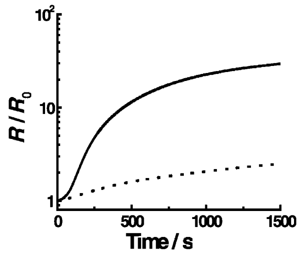

Figure 12. Resistance changes of an HCl-doped nanofiber thin film (solid line) and conventional (dotted line) film upon exposure to 100 ppm ammonia vapor in nitrogen.

Outlook

The conductivity of polyaniline can be affected by many chemical vapors other than just acids and bases. Acidic and basic chemicals change polyaniline's conductivity through alternating the doping level of the emeraldine form of polyaniline. Redox active chemicals could be used to change the inherent oxidation state of polyaniline, thereby changing the degree of conjugation of the polyaniline backbone and the conductivity. Some neutral, redox inactive volatile organic compounds, such as chloroform or toluene, although not able to alter either doping level or the oxidation state, have been reported to affect the conductance of polyaniline films through swelling effects,[33] which induce conductivity changes by modifying the inter-chain hopping of charge carriers. Another possibility is adding functional "guests" into the polyaniline "matrix". This could greatly broaden the scope of polyaniline sensors. Either the guest–matrix complex has new functionality introduced by the guests, or the guest–matrix interaction provides new mechanisms that are sensitive to new targets. One example is trapping enzymes in polyaniline to make it into a biosensor.[8] Other possibilities include mixing polyaniline with materials that catalyze reactions to produce byproducts that are detectable by polyaniline. For all these applications, the use of nanopolyaniline should be beneficial.

The method we developed to make polyaniline nanofibers doesn't depend on the use of specific templates or dopants. It is capable of producing polyaniline nanofibers doped with various acids. The nanofibers can also be modified by using the same chemistry applied to conventional polyaniline. For example, metal nanoparticles such as silver can be loaded onto the nanofibers, forming a uniform polyaniline–metal nanocomposite (Figure 13). Except for the use of a two-phase system, the conditions of our method are similar to that used in the classical synthesis of polyaniline. This effective, yet simple synthetic method should make polyaniline nanofibers a readily accessible model material to facilitate systematic studies on conducting polymer nanostructures, especially for sensor applications.

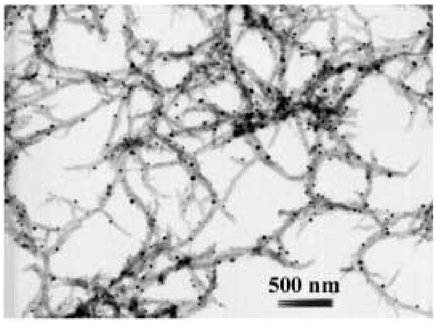

Figure 13. A transmission electron microscopy image of a polyaniline–silver nanocomposite. Silver nanoparticles appear as black dots decorating the polyaniline nanofibers.

Note

The frontispiece appears to be a rocket blasting off above an "ocean" into the sky. However, the ocean is actually a snapshot of the aqueous/organic interface during interfacial polymerization to make polyaniline nanofibers, which is comparable to Figure 4b. Polyaniline turns from blue (undoped) to green (doped) upon doping with acids; therefore, it can be used to detect hazardous HCl waste produced in exhaust plumes from solid rocket motors. The left column of the frontispiece is an SEM image of the nanofibers.

Acknowledgement

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