ACCOUNTS
of chemical research

Polyaniline Nanofibers: A Unique Polymer Nanostructure for Versatile Applications

DAN LI,[‡] JIAXING HUANG,[§] AND RICHARD B. KANER[†,*]

[‡]ARC Centre of Excellence for Electromaterials Science, Department of Materials Engineering, Monash University, Clayton, Victoria 3800, Australia, [§]Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, [†]Department of Chemistry and Biochemistry and California NanoSystems Institute, University of California, Los Angeles, California 90095-1569

RECEIVED ON MARCH 7, 2008

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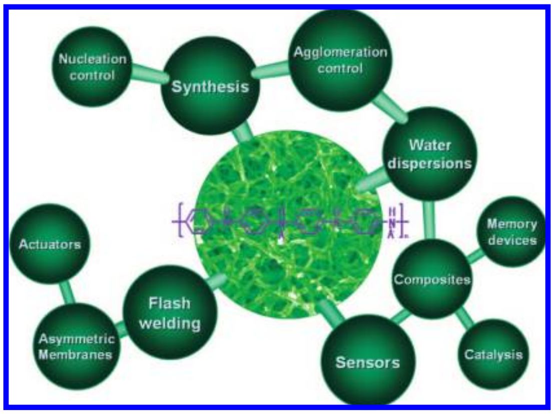

Known for more than 150 years, polyaniline is the oldest and potentially one of the most useful conducting polymers because of its facile synthesis, environmental stability, and simple acid/base doping/dedoping chemistry. Because a nanoform of this polymer could offer new properties or enhanced performance, nanostructured polyaniline has attracted a great deal of interest during the past few years. This Account summarizes our recent research on the syntheses, processing, properties, and applications of polyaniline nanofibers.

By monitoring the nucleation behavior of polyaniline, we demonstrate that high-quality nanofibers can be readily produced in bulk quantity using the conventional chemical oxidative polymerization of aniline. The polyaniline nanostructures formed using this simple method have led to a number of exciting discoveries. For example, we can readily prepare aqueous polyaniline colloids by purifying polyaniline nanofibers and controlling the pH. The colloids formed are self-stabilized via electrostatic repulsions without the need for any chemical modification or steric stabilizer, thus providing a simple and environmentally friendly way to process this polymer. An unusual nanoscale photothermal effect called “flash welding”, which we discovered with polyaniline nanofibers, has led to the development of new techniques for making asymmetric polymer membranes and patterned nanofiber films and creating polymer-based nanocomposites. We also demonstrate the use of flash-welded polyaniline films for monolithic actuators. Taking advantage of the unique reduction/oxidation chemistry of polyaniline, we can decorate polyaniline nanofibers with metal nanoparticles through in situ reduction of selected metal salts. The resulting polyaniline/metal nanoparticle composites show promise for use in ultrafast nonvolatile memory devices and for chemical catalysis. In addition, the use of polyaniline nanofibers or their composites can significantly enhance the sensitivity, selectivity, and response time of polyaniline-based chemical sensors.

By combining straightforward synthesis and composite formation with exceptional solution processability, we have developed a range of new useful functionalities. Further research on nanostructured conjugated polymers holds promise for even more exciting discoveries and intriguing applications.

1. Introduction

Polyaniline was originally known in 1835 as “aniline black”, a term used for any product obtained by the oxidation of aniline.[1] This conducting polymer is well-known for its ease of synthesis, environmental stability, and unique acid/base doping/dedoping and oxidation/reduction chemistry (Figure 1).[1−3] Polyaniline can be readily synthesized by either chemical oxidation or electrochemical polymerization of aniline under mild

Published on the Web 11/06/2008 www.pubs.acs.org/acr
10.1021/ar800080n CCC: $71.50

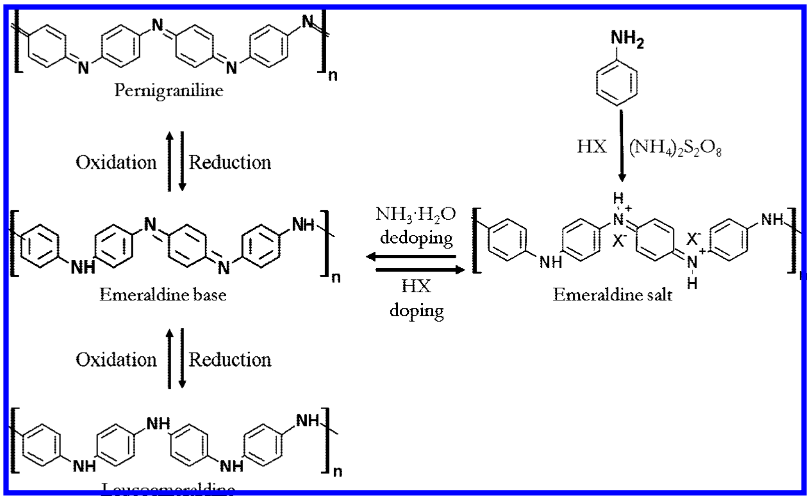

FIGURE 1. Schematic diagram showing the chemical structure, synthesis, reversible acid/base doping/dedoping, and redox chemistry of polyaniline.

conditions.[1−3] In its emeraldine oxidation state, polyaniline becomes electrically conducting when doped with an acid. The doping level can be tuned simply by controlling the pH of the dopant acid solution. The conductivity of polyaniline increases reversibly with doping from the undoped insulating base form ($\sigma \leq 10^{-10}$ S/cm) to the fully doped, conducting salt form ($\sigma \geq 1$ S/cm). Conductivity can also be controlled either chemically or electrochemically by changing the oxidation state (Figure 1).[1−3] The reversible conductivity achieved by doping makes polyaniline a promising material for many applications including in batteries, sensors, actuators, electromagnetic shielding, antistatic coatings, corrosion protection, and electro-optic and electrochromic devices.[1−4] In addition, the ability to control porosity through doping/dedoping could prove useful in separation membranes.[5]

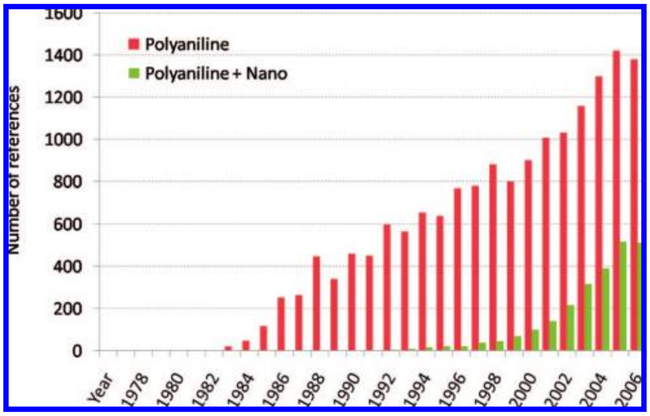

FIGURE 2. The annual number of publications on the subject of "polyaniline" and "polyaniline + nano*", as provided by the search engine of SciFinder Scholar.

Despite being known for over 150 years, research on polyaniline really took off in the 1980s after the birth of conducting polymers as is evident from Figure 2. Research has mainly focused on understanding chemical structure and electronic conduction mechanisms, designing polymerization techniques, and developing chemical or physical modification methods for attempting to make polyaniline processable. With the rapid emergence of nanoscience and nanotechnology in recent years, synthesizing nanostructures of this unique conducting polymer, especially making nanofibers, has attracted growing attention as is shown in Figure 2. The hope is that nanostructured polyaniline will offer better performance or new properties compared with its conventional bulk counterpart. A number of methods for producing polyaniline nanofibers have been reported and summarized in a recent review.[6]

Our group originally discovered that polyaniline nanofibers with controllable diameters can be readily synthesized by an interfacial polymerization method, in which the polymerization is performed in an immiscible organic/aqueous biphasic system.[7,8] No structure-directing agents or templates are required. Fascinated by the simplicity of this method and by a variety of potential applications of polyaniline nanofibers, we have continued studying this nanomaterial with a focus on understanding the formation mechanism and exploring how chemical modifications can be used to enable novel applications. This Account summarizes our recent discoveries with nanostructured polyaniline.

2. Bulk Synthesis of Polyaniline Nanofibers

2.1. Morphological Evolution of Polyaniline Particles in the Conventional Synthetic Reaction. Chemical oxidative polymerization of aniline is one of the traditional methods for synthesizing polyaniline in bulk quantities.[1−3] Green colored polyaniline can be readily obtained after mixing aniline with an appropriate oxidant, for example, ammonium peroxydis-

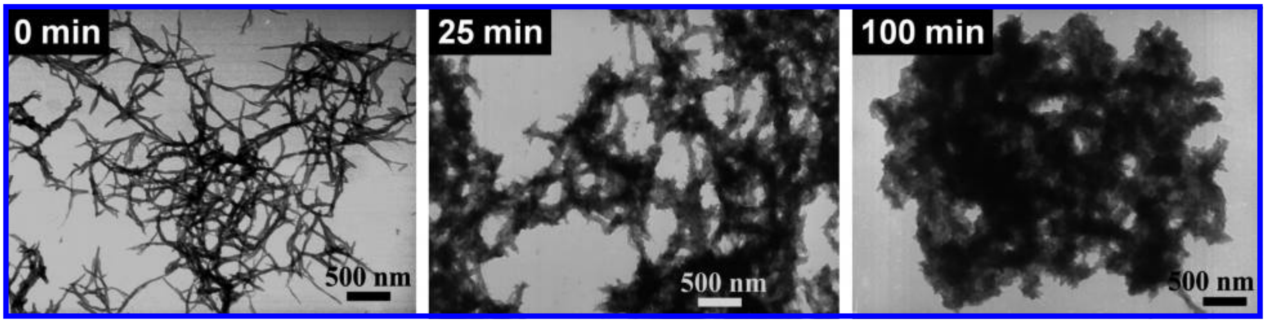

FIGURE 3. Transmission electron microscopy images showing the morphological evolution of polyaniline particles during the conventional synthetic process. The first sample was taken when the green color of polyaniline just became visible.[9]

ulfate, in an acidic solution. Since polymerization of aniline is an exothermic process, it is generally recommended that the reaction be carried out at low temperatures with one reactant slowly added into the other under vigorous stirring.[2] Polyaniline prepared in this way is highly aggregated and rapid sedimentation from solution is generally observed. We have examined how the morphology of polyaniline particles evolves during the traditional chemical oxidative polymerization.[9] As shown in Figure 3, at the initial stage of the polymerization process, when the reaction solution has just turned blue, the collected sample contains almost exclusively well-dispersed nanofibers. As the oxidant solution is gradually added into the aniline solution with vigorous stirring, the obtained nanofibers become thicker and coarser, and the final reaction product contains mostly irregularly shaped agglomerates. This observation indicates that nanofibers are indeed formed in the conventional polymerization process; however, renucleation of more polyaniline on their surface rapidly produces agglomerates as the reaction proceeds. The key to obtaining pure polyaniline fibers is to prevent the subsequent overgrowth of polyaniline on the preformed nanofibers.[9−11]

2.2. Correlating the Shape of Polyaniline Particles with the Nucleation Mode. In order to understand the formation mechanism of irregularly shaped polyaniline agglomerates, we have looked at the reaction process from a viewpoint of classical precipitation theory.[12,13] Polyaniline is a water-insoluble polymer. Therefore the polymerization of aniline is always accompanied by precipitation of the polymerized product. Like all other precipitation processes, the formation of polyaniline is initiated by some nuclei, that is, small molecular aggregates that are formed when their concentration exceeds a specific supersaturation level in solution. The nuclei can be formed spontaneously (homogeneously) in the parent phase, or they can be heterogeneously grown on other species such as reactor surfaces or preformed particles.[12,13] On the basis of a number of experimental observations, for example, that polyaniline films grown on the reactor surfaces are made of granular particulates while the products collected in the bulk reaction solution at the initial stage are nanofibers, we have suggested that the mode of nucleation of polyaniline can be correlated with its particle shape: homogeneous nucleation of polyaniline results in nanofibers, while heterogeneous nucleation leads to granular particulates.[12]

2.3. Heterogeneous Nucleation-Induced Overgrowth and Agglomeration of Polyaniline. Both homogeneous and heterogeneous nucleations occur in the conventional synthetic reaction of polyaniline.[12] As illustrated in Figure 3, at the initial stage of polymerization, there are no heteronuclei available for heterogeneous nucleation and only nanofibers can be formed via homogeneous nucleation. As the polymerization proceeds with time, newly polymerized polyaniline molecules can either grow on the previously formed polyaniline particles via heterogeneous nucleation or continue to precipitate through forming new nuclei via homogeneous nucleation. Under the traditional experimental conditions, it is found that heterogeneous nucleation predominates at the later stage, and new polyaniline molecules prefer to grow on previously formed particles (Figure 4, route I), resulting in the formation of coral-like particles. Additionally, heteronuclei that form at the contact points of the preformed particles can act as a nanoscale glue to link the particles together, leading to irreversible agglomeration.[12,13]

2.4. Strategies To Attain High-Quality Polyaniline Nanofibers. Although pure polyaniline nanofibers can be obtained by terminating the polymerization of aniline before secondary growth starts, the yield of nanofibers is generally too low to be suitable for large-scale synthesis. The synthesis should be more efficient if heterogeneous nucleation can be suppressed throughout the whole polymerization process, which will allow polyaniline nanofibers to form continuously via homogeneous nucleation (Figure 4, route II).

A faster rate of polymerization appears to favor homogeneous nucleation.[12] Since only homogeneous nucleation is possible in bulk solution, a higher transient concentration of

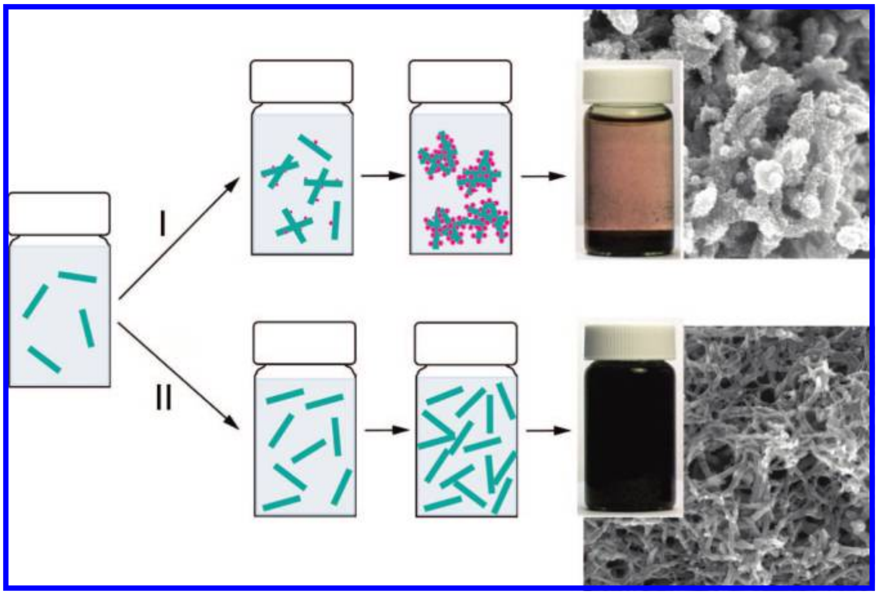

FIGURE 4. Schematic illustrations and images showing how the nucleation mode of polyaniline is related to the shape and aggregation of the resulting particles during the synthetic process.[12,13] The fibers and dots represent polyaniline that results from homogeneous and heterogeneous nucleation, respectively. At the initial stage, polyaniline nanofibers form exclusively. Subsequently, (I) if heterogeneous nucleation is favored, new molecules will grow on the preformed nanofibers, leading to the formation of thicker and agglomerated particles; (II) if heterogeneous nucleation is suppressed and homogeneous nucleation is predominant, well-dispersed polyaniline nanofibers will be continuously produced. Typical SEM images of the products from the two different routes are presented next to the reaction vials.

polyaniline molecules will facilitate the formation of more homogeneous nuclei at the beginning of precipitation. Moreover, if polyaniline molecules are produced rapidly, then it is more likely that these embryonic nuclei will evolve to create homogeneous nuclei since it takes time to diffuse to heterosites. Therefore experimentally, both rapid mixing of the two reactant solutions and conducting the reaction at elevated temperatures are beneficial for generating nanofibers since they enable polyaniline molecules to form quickly. As shown in Figure 5, polyaniline fibers obtained at 0 °C have rough surfaces and precipitate rapidly from the reaction solution. In contrast, when the reaction is run at 60 °C, there are almost no granular particulates in the product.

Another important experimental parameter that has a dramatic effect on the nucleation behavior of polyaniline is mechanical agitation, for example, stirring or shaking.[12] Mechanical stirring is found to greatly favor heterogeneous nucleation.[12,13] For example, the thickness of *in situ* deposited films on the reactor surface grown via heterogeneous nucleation increases as stirring speeds up. A stirred reaction always results in a higher percentage of larger particle sizes than a nonstirred reaction.[12] Particularly, we have found that if presynthesized polyaniline nanofibers are added in the polymerization solution of aniline and the reaction is vigorously stirred upon the addition of the oxidant, most polyaniline will grow on these nanofiber seeds. However, if the reaction solution is kept still, new polyaniline nanofibers will form separately as if the preadded nanofibers were absent (Figure 6).

Taking all these experimental factors into account, one will find that it is very easy to prepare polyaniline nanofibers with a high yield: high-quality nanofibers can be readily obtained in large quantities by rapidly mixing aniline with an appropriate oxidant in an aqueous acidic solution at room temperature or above and then allowing the polymerization to proceed to completion in the absence of mechanical agitation.[9,12,13]

2.5. Diameter Control of Polyaniline Nanofibers. The diameter of the nanofibers is found to be related to the acid used in the polymerization.[7−9] The average diameter of nanofibers produced with hydrochloric acid is about 30 nm, while those made in camphorsulfonic acid approach 50 nm, and those synthesized in perchloric acid are around 120 nm. Other reaction parameters such as temperature, reaction time, and concentration of the aniline and oxidant appear to have little effect on the sizes of the resulting fibers. The growth of polyaniline nanofibers appears to be a self-limiting process that leads to their relatively narrow diameter distribution.

2.6. Nanofibers of Polyaniline Derivatives and Other Conducting Polymers. We have tested a number of substituted anilines to see whether nanofibers of polyaniline derivatives can be obtained using the conventional chemical oxidative polymerization. The morphology of the resulting polyaniline particles is found to be strongly dependent on

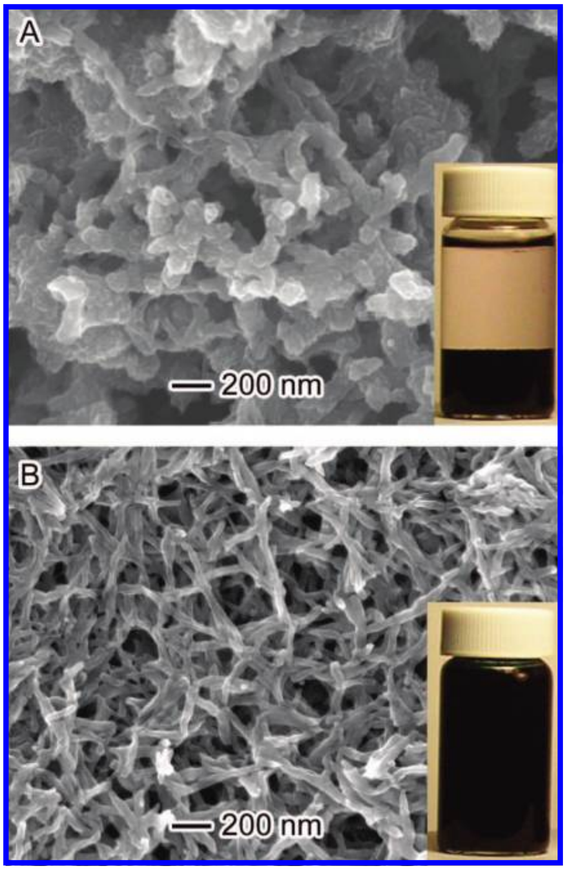

FIGURE 5. SEM images of polyaniline synthesized by rapidly mixing an aniline solution with an oxidant at 0 (A) and 60 °C (B). As shown in the insets, polyaniline synthesized at 0 °C precipitates quickly, while that synthesized at 60 °C will remain well suspended.[12]

both the substituent groups used and their positions along the polymer backbone. Most polyaniline derivatives, unfortunately, do not exhibit a well-defined fibrillar shape if prepared under the normal synthetic conditions.[11] However, if an aniline oligomer is added into the reaction mixture to accelerate the reaction, nanofibers of polyaniline derivatives such as alkyl, methoxy, fluoro, and thiomethyl substituted polyanilines can be readily synthesized.[14] Interestingly, we have also found that nanofibers of other conducting polymers such as polypyrrole can be readily prepared by adding an oligomer, for example, bipyrrole, into the conventional polymerization solution to accelerate the reaction.[15] These added oligomers likely promote homogeneous nucleation.[14,15]

3. Properties and Applications of Polyaniline Nanofibers

3.1. Solution Processability of Polyaniline Nanofibers. As shown in Figure 3, polyaniline synthesized using the conventional chemical method is highly agglomerated. The resulting large particles are difficult to disperse and therefore unsuitable for most applications. Traditional methods to make soluble or dispersible polyaniline involve chemical functionalization, copolymerization, or emulsion/dispersion polymerizations in the presence of alien surfactants, but all involve trade-offs in terms of cost, purity, scalability, or conductivity. The successful production of polyaniline nanofibers has enabled us to develop a convenient and low-cost strategy to improve the solution processability of polyaniline.[16] Polyaniline fibers prepared using the above method are very small in size. They form interconnected networks with well-separated segments (owing to homogeneous nucleation). Most importantly, they are positively charged in the doped state. All these factors make it possible to prepare colloidal dispersions through electrostatic stabilization without the need for any foreign stabilizers such as surfactants or polymers. We have found that stable aqueous colloids of doped polyaniline nanofibers can be readily obtained so long as free electrolytes are removed from the dispersion, and the pH is controlled to around 2.6 (Figure 7A).[16]

The ability to form stable polyaniline colloids makes it very convenient to process this conducting polymer using low-cost conventional solution-phase processing techniques. Continuous thick films or coatings can be obtained simply through spraying or casting (Figure 7B). Additionally, by taking advantage of the characteristic that polyaniline nanofibers dispersed at an optimal pH are positively charged, we have demonstrated that ultrathin nanofiber films can be spontaneously formed on a negatively charged substrate surface through an electrostatic self-assembly process (Figure 7C). This also makes layer-by-layer epitaxy possible by alternately exposing a nanofiber film to solutions containing first negatively and then positively charged nanoparticles.

The strategy we have developed for producing stabilizer-free polyaniline dispersions appears to be applicable to other nanostructures as well. For example, we have recently demonstrated that chemically prepared graphene nanosheets can also form stable aqueous dispersions without the need for other stabilizers, making this unique carbon nanostructure solution-processable.[17]

3.2. Improved Performance with Polyaniline Nanofiber-Based Chemical Sensors. The development of high-performance chemical sensors is of great importance in environmental protection and homeland security.[18−26] Polyaniline is a promising material for chemical sensors since its conductivity is highly sensitive to many chemical vapors at the parts per million level or less through several different mechanisms including doping/dedoping, reduction/oxidation, swell-

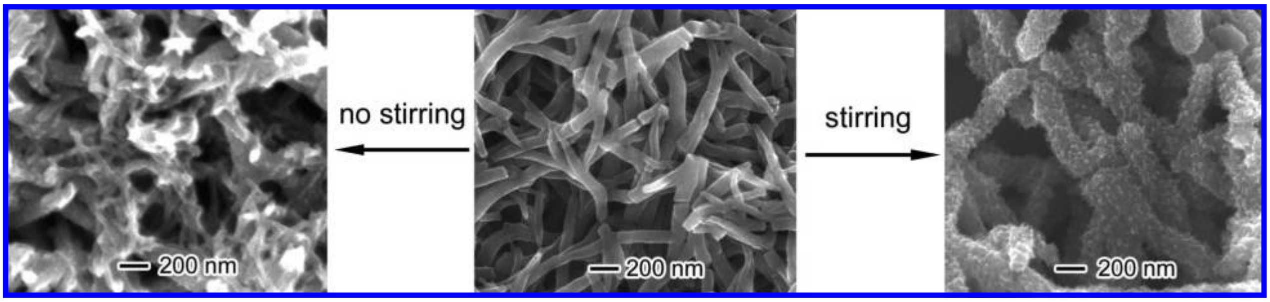

FIGURE 6. SEM images of polyaniline samples prepared in the presence of previously prepared polyaniline nanofiber seeds of ~120 nm in diameter (middle). The reactions are carried out without stirring (left) and under rapid stirring at 1100 rpm (right), respectively.

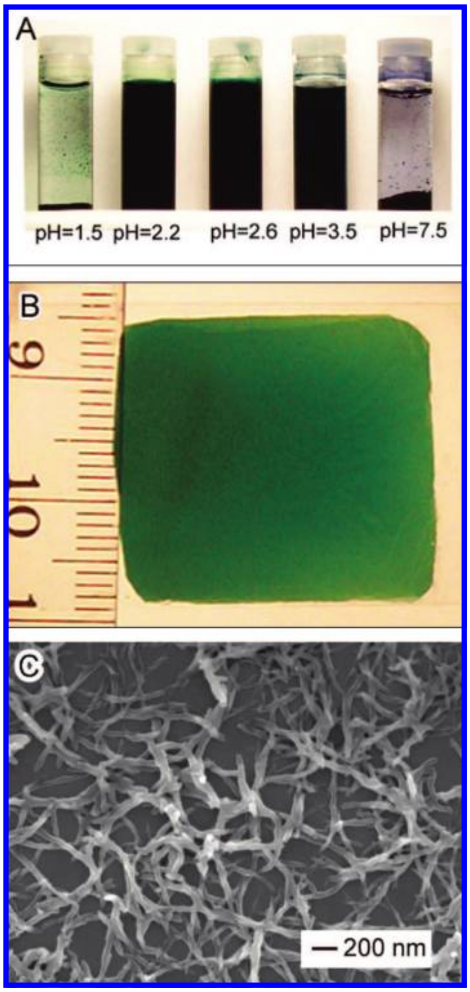

FIGURE 7. (A) Polyaniline nanofiber dispersions (1 mg/mL) at different pHs after standing for 15 h at room temperature, (B) photograph of a film cast on a glass slide from a polyaniline nanofiber colloid, and (C) SEM image of a thin layer of nanofibers spontaneously adsorbed onto a silicon wafer after being immersed in a polyaniline colloid.[16]

ing, and altering the polymer conformation.[18−26] For example, many toxic chemicals either are acids or rapidly hydrolyze in humid environments to form acids, such as HCl, HF, HNO_3, PCl_3, and BF_3. These acids can be detected by polyaniline nanofiber-based sensors directly because they can protonate the emeraldine base form of polyaniline and increase its conductivity. This makes polyaniline promising for detecting chemical warfare agents, many of which produce strong acids upon hydrolysis.[27] Conversely, the protonated emeradine salt form of polyaniline can be used to detect basic vapors, such as NH_3 or organic amines. These gases/vapors can deprotonate the polymer and decrease its conductivity. In addition to these gases, redox active chemicals, such as Cl_2, F_2, Br_2, I_2, N_2H_4, NO_x, and SO_x can change the inherent oxidation state of polyaniline, which can also result in large changes in conductivity.

A common device platform for constructing such sensors is a chemiresistor, which can be fabricated by drop-casting a small amount of a polyaniline nanofiber dispersion onto either interdigitated or gap electrodes.[19−24] Surface acoustic wave (SAW) transducers using polyaniline nanofibers as active sensing materials can also be built by simply depositing the nanofibers on the device surface.[25,26] Of significance is that the unique three-dimensional porous structure of polyaniline nanofiber films allows chemical vapor to rapidly access essentially all nanofibers upon exposure, leading to superior sensing performance compared with conventional bulk films (Figure 8). A variety of chemical vapors, including hydrochloric acid, ammonia, organic amines, hydrazine, chloroform, methanol, and hydrogen sulfide, have been tested. Significantly enhanced performance of nanofiber films over conventional materials is observed in both sensitivity and response time.

3.3. Flash Welding of Polyaniline Nanofibers. Besides using nanostructured polyaniline to improve the performance of chemical sensors, our group has discovered another unique nanoscale phenomenon associated with polyaniline nanofibers.[28] Polyaniline as a conjugated polymer has strong light-absorbing properties in the visible region due to the π to π^* transition. When exposed to light, polyaniline converts most of the absorbed energy into heat. For a bulk dense polyaniline film, the generated heat can be rapidly dissipated throughout a large volume and to its surroundings so that any asso-

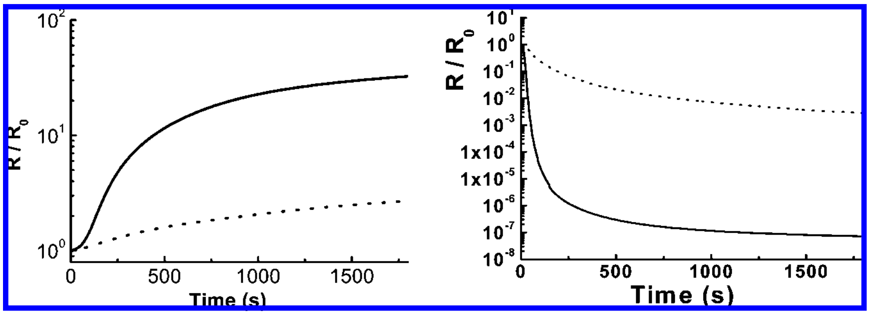

FIGURE 8. Response of a nanofiber film (solid line) and a conventional film (dotted line) upon exposure to 100 ppm NH_3 vapor (left) and 100 ppm HCl vapor (right).[20] Doped and dedoped polyaniline were used to detect NH_3 and HCl, respectively. R/R_0 is the resistance (R) normalized to the initial resistance (R_0) prior to gas exposure.

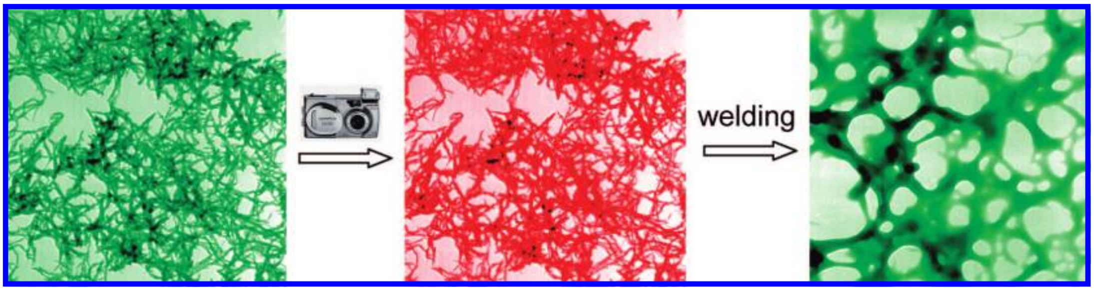

FIGURE 9. Colored TEM images of polyaniline nanofibers showing an enhanced photothermal effect. Green polyaniline nanofibers (left) are locally heated on exposure to a camera flash (middle). The heating immediately leads to the melting of the nanofibers (right) (Adapted from ref 28).

ciated rise in temperature is moderate, as is normally observed.[28,29] However, when a porous film made of polyaniline nanofibers is illuminated, the generated heat will be trapped within the individual nanofibers and dissipate slowly since the surrounding air is a very poor heat conductor. If the light is sufficiently intense, for example, a camera flash, the inability to dissipate heat effectively will cause a rapid temperature rise in the fibers, which can lead to instantaneous welding or even burning of the nanofibers (Figure 9). Under flash irradiation of moderate intensity, polyaniline nanofibers will rapidly "melt" to form a smooth and continuous film. We refer to this phenomenon as flash welding. This should be a general phenomenon for nanomaterials with characteristics of high absorbance, high photothermal conversion efficiency, and a phase change before structural breakdown.

3.4. Applications of Flash Welding. Flash welding of polyaniline nanofibers not only provides a nice example of how things can change at the nanoscale but also offers a new technique for processing polyaniline into potentially useful structures. For example, when a thick nanofiber film is exposed to a camera flash, only the exposed side is welded, while the unexposed side remains intact. Therefore, a free-standing asymmetric membrane can be created directly from a nanofiber film (Figure 10A). A polyaniline nanofiber film can also be easily patterned to form selected nanofiber and melted regions by applying a photomask on top of the film followed by exposure to a light flash.[28] Additionally, if polyaniline nanofibers are mixed with other polymer particles (e.g., polystyrene beads), the heat generated during flash irradiation can weld polyaniline and other polymers together to form composites or simply be used for welding nonconjugated polymers to each other.[28]

Asymmetric polyaniline nanofiber films formed by flash welding offer an interesting application as monolithic actuators.[30] An actuator is a device that makes use of electrical, chemical, or other forms of energy to induce motion. As shown in Figure 10A, a film welded on its surface only possesses an asymmetric cross-section, making it an intrinsically bilayer-type monolithic actuator. When the bilayer film of dedoped polyaniline is exposed to an acid, the nanostructured portion of the film expands as a result of charge repulsion and incorporation of anionic dopants into the film (Figure 10B). Because the welded side of polyaniline is quite dense and partially cross-linked due to the flash-induced high temperature, the welded side is much less expandable than the unwelded nanofiber side. The asymmetric expansion thus results in the bending and coiling of the film toward the welded side when exposed to an acid solution (Figure 10C). The porous structure in the unwelded nanofiber side allows the ions to quickly diffuse into individual fibers, leading to relatively rapid actuation. An approximately 720° curling from the original position of a 3 cm length asymmetric film can be completed

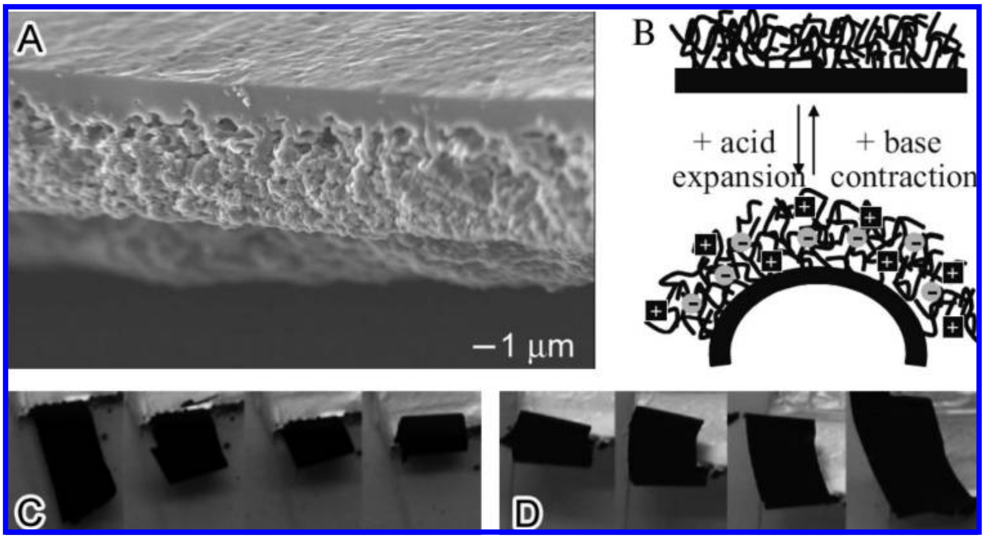

FIGURE 10. (A) An SEM image of a fractured cross-section of a polyaniline nanofiber film with the upper layer flash welded, (B) schematic showing the actuation of the as-formed asymmetric film upon exposure to an acid, (C) photographs showing the actuation of a flash-welded, dedoped polyaniline film when immersed in an acid—the four images taken at 0, 10, 15, and 20 s show that the asymmetric film coils upon itself two full revolutions, and (D) after rinsing in water, exposure to a basic solution reverses the process causing the film to unscroll as seen after 0, 10, 15, and 20 s.[30]

within 20 s. The chemo-mechanical actuation is reversible. Placing the acid coiled flash welded film into a basic solution can reverse the coiled expansion to its original nonswollen form by the removal of the repulsive charges, dopant ions, and solvent through dedoping (Figure 10D). A continuous single component bending/curling actuator has several advantages over conventional dual component, bimorph actuators including ease of synthesis, large degree of bending, patternability, and no delamination.[30]

4. Modification of Polyaniline Nanofibers for Novel Applications

4.1. Facile Routes to Modifying Polyaniline Nanofibers. As discussed in the following sections, the potential of polyaniline nanofibers can be significantly expanded by coupling pristine polyaniline nanofibers with other functional materials through chemical or physical modification. Polyaniline nanofibers are highly dispersible in water under the proper conditions as discussed in Section 3.1. Polyaniline composites can be readily formed by simply mixing nanofibers with other water-soluble functional materials, for example, molecules, nanoparticles, or polymers, in water.[21,31] For water-insoluble materials, compositing can be achieved by infiltration of a solution containing suitable materials into a dried nanofiber film. The unique three-dimensional porous structure of polyaniline nanofiber films allows the incorporated materials to be directly in contact with individual nanofibers, which offers an immediate advantage over conventional bulk polyaniline.

The unique reduction/oxidation chemistry of polyaniline is particularly useful for modifying these nanofibers. For example, we have demonstrated that some metal salts, such as those of Au, Pt, and Pd, can be reduced by the emeraldine base form of polyaniline to produce metal nanoparticles inside or on the surface of the nanofibers, while polyaniline is oxidized to a higher oxidation state, pernigraniline.[32−34] The oxidized polyaniline can then be reduced back to the emeraldine oxidation state. By repetition of this process or adjustment of concentration, temperature, and reaction time, the size and density of the deposited nanoparticles can be controlled. Furthermore, a combination of different metals can be introduced into the same fibers by sequentially exposing the fibers to different metal ions.

4.2. Modification of Polyaniline Nanofibers for Chemical Sensing. Although pure polyaniline nanofibers are a versatile material for chemical sensing, several challenges still remain, including low sensitivity to certain analytes and poor selectivity. Modification of polyaniline nanofibers with selected additives may provide an effective strategy to addressing these issues. If a target analyte has weak interactions with polyaniline, the sensitivity can be improved by incorporating suitable functional dopants or catalysts to effectively convert target vapor molecules into easily detected species. For example, solution doping experiments show that it takes several

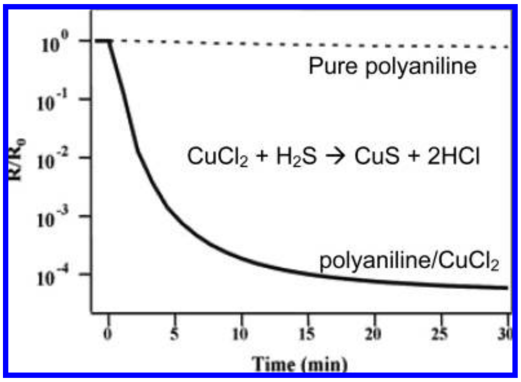

FIGURE 11. Response of a dedoped polyaniline nanofiber film to H_2S with (solid curve) and without (dashed curve) incorporated copper chloride ($CuCl_2$). In the presence of the salt, a strong acid (HCl) is generated upon exposure to H_2S (inset). The four order-of-magnitude enhancement in sensitivity is due to doping caused by the *in situ* generated HCl.[21]

weeks for a saturated H_2S solution to even partially dope polyaniline nanofibers since hydrogen sulfide is a weak acid. Therefore, using pristine polyaniline to detect H_2S is very difficult. Given that H_2S reacts rapidly with many metal salts, for example, $CuCl_2$, to form a metal sulfide precipitate and generate a strong acid (i.e., HCl), we have mixed $CuCl_2$ with polyaniline nanofiber films. When the composite film is exposed to H_2S vapor, it becomes doped by the HCl generated as a byproduct of CuS formation within a few seconds. The sensitivity of polyaniline nanofibers to H_2S vapor can thus be improved by 4 orders of magnitude (Figure 11).[21]

The ease of altering the sensing characteristics of polyaniline nanofibers through forming composites could make it very convenient to enhance the selectivity of polyaniline-based chemical sensors as well. By incorporation of different materials into the nanofibers, an array of sensors consisting of polyaniline nanofibers but modified by different materials can be easily fabricated. In such arrays, each sensor has a different response to a given analyte. Thus, by using a neural network technique,[35] both the type and concentration of a specific target can be recognized.

4.3. Polyaniline Nanofiber/Metal Nanoparticle Memory Devices. Modification of pristine polyaniline nanofibers provides an efficient means not only to enhance existing functionalities but also to create new ones. For example, using gold nanoparticle decorated nanofibers (Figure 12A) as an active layer sandwiched between two aluminum electrodes, we have discovered that gold/polyaniline nanofibers possess a remarkable electrically switchable bistability, which is ideal for nonvolatile flash memory devices.[32,33] With ~2 nm gold particles grown on polyanline nanofibers, the device can be switched from the off- to the on-state at ≥3 V with a switching time of ≤25 ns. This produces an abrupt increase in current of more than 3 orders of magnitude (Figure 12B). The device can be switched back to the off-state at less than or equal to −5 V. The device is stable in both states and switching between these two states can be repeated numerous times without any obvious decay. Control experiments confirm that both polyaniline and gold nanoparticles are important. The absence of either results in the disappearance of the bistable switching behavior. Raman and X-ray photoelectron spectroscopic analyses suggest that the switching properties of the composite are based on an electric-field induced charge transfer between the polyaniline nanofibers and the gold nanoparticles.[33] The charge can be stably trapped on the nanoparticles when the electric-field is removed. Both the charge transfer and the stability of the devices are related to the nanoscale dimensions of the materials and the interface between the gold nanoparticles and the polyaniline nanofibers.

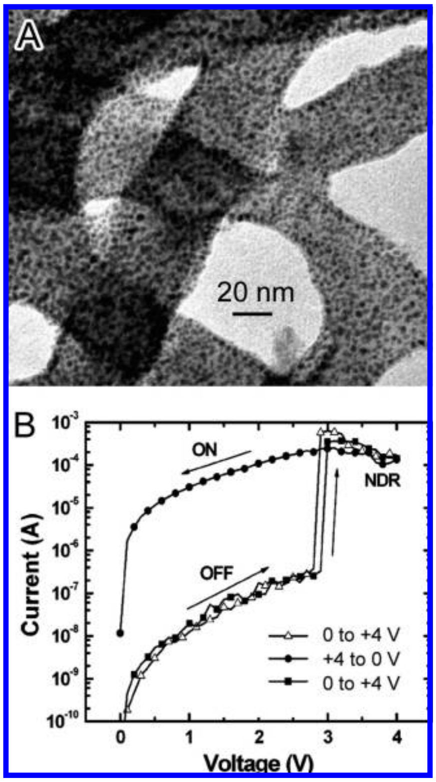

FIGURE 12. (A) TEM image of a polyaniline/gold nanocomposite prepared by exposure of polyaniline nanofibers to chloroauric acid under controlled conditions[32] and (B) current−voltage characteristics of an electronic device in which the polyaniline/gold composite is sandwiched by two aluminum electrodes. The potential is cyclically scanned from 0 to +4 V.

4.4. Polyaniline Nanofiber/Metal Nanoparticle Composites for Catalysis. The potential use of polyaniline nanofibers is not limited to functional materials in novel electronic devices. As a relatively inexpensive and scalable nanomaterial that can incorporate metal nanoparticles, polyaniline nanofibers could act as potentially useful nanoscale support material for catalysis. We have shown that palladium nanoparticles supported on polyaniline nanofibers prepared simply by exposing polyaniline nanofibers to a palladium salt can be used as an active catalyst for Suzuki coupling between, for example, aryl chlorides and phenylboronic acid in water at relatively low temperatures.[34] The polyaniline nanofibers appear to play a multifunctional role in this catalyst system: as reducing agent to produce Pd nanoparticles, as a stabilizer to prevent the agglomeration of Pd nanoparticles, and as a water-dispersible catalyst support.

5. Concluding Remarks

Through the examples demonstrated in this short review, we hope the reader finds that polyaniline nanofibers are a very useful polymer nanostructure with many unique features combining the following. (1) Ease of synthesis: The synthesis can be readily accomplished under mild conditions in any chemical synthetic laboratory and the production of polyaniline nanofibers is reproducible, scalable, and inexpensive. (2) Exceptional solution processability: Polyaniline nanofibers are highly dispersible in water, which allows the use of low-cost conventional solution processing techniques to process this nanostructure into a variety of usable forms such as composites and films. (3) Exceptional functionality: Polyaniline nanofibers possess the same functionalities as bulk conventional polyaniline, such as tunable conductivity, electrochemical activity, electrochromic behavior, and capability for acid/base doping/dedoping and oxidation/reduction. For many applications, such as chemical sensing and water dispersability, nanofibrillar polyaniline performs much better than its bulk counterpart. Additionally, polyaniline nanofibers exhibit some new effects that are only available at the nanoscale such as molecular memory and an unprecedented photothermal effect. (4) Ease of forming composites to create new functionalities by simple chemical reactions or physical mixing. All these characteristics suggest that polyaniline and other conjugated polymeric nanofibers[15,36] will likely lead to even more exciting future discoveries and intriguing applications.

This research has been funded by NSF Grant DMR 0507294 (R.B.K.), the Australian Research Council (D.L.), and Northwestern University new faculty start up fund (J.H.). R.B.K. is indebted to those individuals who have carried out this work including his group members C. Baker, J. D'Arcy, R. Kojima, B. Shedd, Prof. K. Shin, and H. Tran and his collaborators on sensors, Dr. B. H. Weiller and Dr. S. Virji (The Aerospace Corp.) and Prof. W. Wlodarski and Prof. K. Kalantar-Zadeh (RMIT); on actuators, Prof. G. G. Wallace, Prof. G. M. Spinks, Dr. P. C. Innis, and Dr. P. G. Whitten; on catalysis, Prof. P. Diaconescu; and on memory devices, Prof. Y. Yang and Dr. R. Tseng.

BIOGRAPHICAL INFORMATION

Dan Li received a Ph.D. in materials physics and chemistry from the University of Electronic Science and Technology of China in 1999. After several years as a research fellow at the Nanjing University of Science and Technology, the University of Washington, UCLA, and the University of Wollongong, he is now an Associate Professor/Queen Elizabeth II Fellow at the Department of Materials Engineering, Monash University, in Melbourne, Australia. His current research interests are synthesis, processing, assembly, and applications of novel functional nanostructures, especially graphene-based materials.

Jiaxing Huang received a Ph.D. in chemistry from the University of California, Los Angeles (UCLA), in 2004. He then earned a Miller Research Fellowship to carry out postdoctoral studies at the University of California, Berkeley. Dr. Huang joined the Materials Science and Engineering Department at Northwestern University as an Assistant Professor in 2007. His work on conducting polymer nanostructures has been recognized with a Prize for Young Chemists from the International Union of Pure and Applied Chemistry (IUPAC) and the National Starch & Chemical Award in Polymer Science and Engineering from the American Chemical Society. He also earned an Inventor's Recognition Award from the Microelectronics Advanced Research Corporation. Dr. Huang's current research focuses on the chemical synthesis and assembly of nanostructured materials for tailoring properties and applications; examples include anisotropic plasmonic nanostructures, high-performance conducting polymers, and controlled assembly of soft nanomaterials.

Richard B. Kaner received a Ph.D. in inorganic chemistry from the University of Pennsylvania in 1984. After carrying out postdoctoral research at the University of California, Berkeley, he joined the University of California, Los Angeles (UCLA), in 1987 as an Assistant Professor. He was promoted to Associate Professor with tenure in 1991 and became a Full Professor in 1993. Professor Kaner has received awards from the Dreyfus, Fulbright, Guggenheim, and Sloan Foundations, as well as the Exxon Fellowship in Solid State Chemistry and the Buck-Whitney Research Award from the American Chemical Society for his work on refractory materials including new synthetic routes to ceramics, intercalation compounds, superhard materials, graphene, and conducting polymers.

FOOTNOTES

*To whom correspondence should be addressed. E-mail: kaner@chem.ucla.edu.

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