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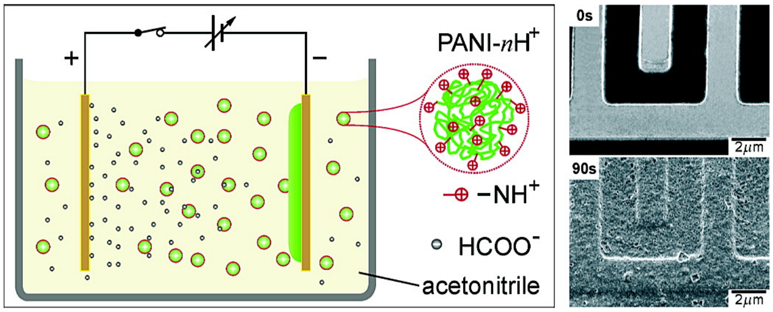

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Controlled Electrophoretic Patterning of Polyaniline from a Colloidal Suspension

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Abstract: We present a method for controlled deposition of polyaniline from colloidal suspensions. Stable suspensions of polyaniline colloids (~115 nm in diameter) were formed by dispersing polyaniline/formic acid solution into acetonitrile. It was demonstrated that the positively charged polyaniline colloids can be electrophoretically deposited onto various substrate materials such as platinum and ITO, forming continuous ultrathin films. We examined the film morphology, as well as the effects of process parameters, such as deposition time, colloid concentration, and applied voltage, on the deposition efficiency. Furthermore, the efficacy of the technique was illustrated by electrophoretically patterning polyaniline thin films onto selected individual micrometer-scale sensing elements within a microfabricated sensor array, and by further demonstrating its sensitivity to gaseous analytes including water and methanol.

I. Introduction

Conducting polymers are a unique class of organic materials that exhibit electrical and optical properties of metals or semiconductors.[1] They offer great prospects for practical applications due to their unparalleled architectural diversity and flexibility, inexpensiveness, and ease of synthesis. To some extent, the field of organic conductors has evolved from a novel science into a resource for new technologies. Existing and emerging molecular electronics that are based on conducting polymers include chemical and biological sensors, field-effect transistors, integrated circuits, light emitting diodes, and solar cells.[2−7] Recent advances in nanostructures and devices have further extended the interest in this dynamic field. Among all of the conducting polymers, polyaniline is probably the most widely studied because it has a broad range of tunable properties derived from its structural flexibility. It can be conveniently synthesized either chemically or electrochemically.[8−10] Various polyaniline derivatives, copolymers, and blends or composites have been investigated.[11−15] Most intriguingly, low-dimensional nanostructures of polyaniline in various shapes and forms, for example, nanowires, nanofibers, nanoshells, and nanotubes, have been produced.[16−20] Yet like many other electrically conducting polymers, polyaniline is hard to process due to its insolubility in common solvents. Despite all of the progress, polyaniline's limitation in processibility persists, preventing it from fully reaching its practical potential. Especially for device applications, with features increasingly going down in size, there is a pressing need for a practical method capable of reproducibly integrating polyaniline onto selected device structures with precision and control.

The formation of polyaniline dispersions has been exploited as an effective method of getting around the limitations of processibility for this material. After all, a stable colloidal suspension has an indistinguishable appearance from a true solution, and most importantly it can be handled and applied similarly. In previous work, the colloidal suspensions of polyaniline have been mostly produced by a process that is referred to as dispersion polymerization.[21] The dispersion polymerization of polyaniline is carried out in an aqueous mixture containing aniline monomers and oxidants with the presence of a suitable steric stabilizer. As the aniline monomers polymerize, a surface layer of a steric stabilizer attaches to the precipitates of polyaniline particles, not only preventing further polymerization of aniline monomers onto the particles, but also protecting the particles from aggregation. Hence, a stable dispersion of polyaniline colloidal particles can be obtained.

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Common oxidants such as $FeCl_3$ or $(NH_4)_2S_2O_8$, along with a wide variety of steric stabilizers ranging from water-soluble polymers and inorganic oxides to surfactants, have been used.[22−26] The colloids prepared from dispersion polymerization have a "core−shell" structure. The core is mainly composed of insoluble polyaniline, and it is coated with a shell of either water-soluble polymeric or colloidal stable ultrafine inorganic steric stabilizers. Although a polyaniline chain in its emeraldine salt form is a polymeric cation, the charge-stabilization contribution from the core is secondary to the steric stabilization that originates from the shell. One drawback of preparing polyaniline colloidal suspensions through dispersion polymerization is that the processibility is gained through compromising the purity of the polyaniline. Additionally, having a layer of insulating polymer or oxide on the surface of a polyaniline core will have unintended effects on the surface and interfacial properties of polyaniline, which may be deleterious.

Another alternative is to immobilize polyaniline onto template materials that can be more easily handled. One example of such template materials is polystyrene beads. Micrometer-sized latex beads are generally used with polyaniline coatings formed through chemical or electrochemical polymerization, or electrostatic layer-by-layer assembly.[20,27−31] In comparison to polyaniline colloidal particles prepared by dispersion polymerization, these electrically conductive particles have a similar "core−shell" structure, but are inverted with the shell being the conducting polyaniline while the core consists of a single insulating polystyrene bead. Monodispersed polystyrene spheres with a polyaniline shell can be packed onto substrates and assembled into well-ordered structures.[20,27] The polystyrene core can be removed later by solvents such as toluene or tetrahydrofurane, so that the interference from the template materials can be minimized. However, the extra removal step will inevitably extend the already lengthy processing procedure.

More recently, inkjet-printing[32−34] and electrospinning[17,35−37] have emerged as attractive patterning techniques for conjugated polymers. However, the inkjet-printing technique is hampered by its resolution limit (~50 μm).[32] Electrospinning has been extensively explored as a method capable of drawing fibers from polymer solutions and simultaneously integrating them onto microfabricated structures. It has been demonstrated that nanofibers with sub-30 nm diameter can be electrospun from polyaniline/polyethylene-oxide blends.[36] Apparently, the fabricated nanofibers have the insulating polyethylene-oxide as an impurity, giving rise to substantially lower conductivity in comparison to pure bulk materials, especially for the fibers with smaller diameters. In fact, electrospun nanofibers with diameters lower than 15 nm were found to be insulating.[36] Above all, excessively high voltages (4000−25 000 V) are required to extract a polymer liquid jet (that dries to form a fiber) from the polyaniline blend solution.[35−37] Therefore, this technique is not entirely practical.

In this paper, we report a convenient method for forming polyaniline colloidal suspensions. We also demonstrate that these polyaniline colloids can be electrophoretically deposited onto various substrate materials. Furthermore, we use NIST microhotplate sensor arrays to illustrate the capability of the electrophoretic technique for patterning polyaniline onto selected microfabricated device features with excellent control.

II. Experimental Section

Polyaniline was electrochemically synthesized from 0.1 M aniline in 2 M HCl aqueous solution by cycling in the potential range from 0 to 850 mV (vs an Ag/AgCl reference electrode) at a scan rate of 10 mV/s. The electrochemically synthesized polyaniline was then converted into its emeraldine base form by soaking in a concentrated ammonium hydroxide solution. The polymer was filtered and washed with deionized water and methanol, and then dried in a vacuum oven. A stock solution of polyaniline (1 mg/mL) was prepared by dissolving polyaniline powder in formic acid. Polyaniline colloidal suspensions of various concentrations were prepared by adding polyaniline stock solution into acetonitrile in various volume ratios. For example, to make 10 mL of 10 mg/L polyaniline suspension, 100 μL of the stock solution was mixed into 9.9 mL of acetonitrile. Gentle shaking or brief sonication of the mixture for a few seconds is sufficient to fully disperse the polyaniline colloids. Particle size distribution of the polyaniline colloids was characterized by dynamic light scattering with a Malvern Zetasizer (model # 3000HS). The electrophoretic deposition was carried out in a small Teflon cell with 5 mL capacity. A Sorensen 600W programmable power supply (model # DLM 60-10) was used to supply DC voltages. Film thickness was measured using a Dektak 6M profilometer. Specular FTIR spectra were measured from films deposited on platinum-coated silicon substrates using a Biorad FTS7000 spectrometer equipped with a reflectance stage. Optical absorption spectra were obtained from films deposited on ITO-coated glass substrates using a Perkin-Elmer Lamda Bio-20 UV/vis spectrometer. Scanning electron micrographs were taken with a Hitachi S-4000 microscope. All solvents were purchased from Sigma-Aldrich and used as received. ITO-coated glass substrates (15 Ω/□) were obtained from Structure Probe Inc.; platinum substrates were prepared by sputtering 2000 Å of platinum on a thermal oxide coated silicon wafer with 300 Å of titanium as the adhesion-promoting layer. The microhotplate sensor arrays were designed at NIST, produced in wafer runs at MIT Lincoln Laboratories, and then micromachined and packaged at NIST. The array was mounted and wire-bonded to a 40-pin dual in-line package to provide electrical connectivity to the contacts and heaters. The device was encapsulated to electrically isolate the wirebonds and bonding pads.

III. Results and Discussion

A. Polyaniline Colloidal Suspension. As schematically illustrated in Figure 1, the polyaniline colloidal suspension was prepared by first dissolving the emeraldine base form of polyaniline in formic acid, and subsequently dispersing the polyaniline/formic acid solution into acetonitrile. The key aspect of generating a polyaniline colloidal suspension lies in the unique combination of formic acid and acetonitrile. First, the

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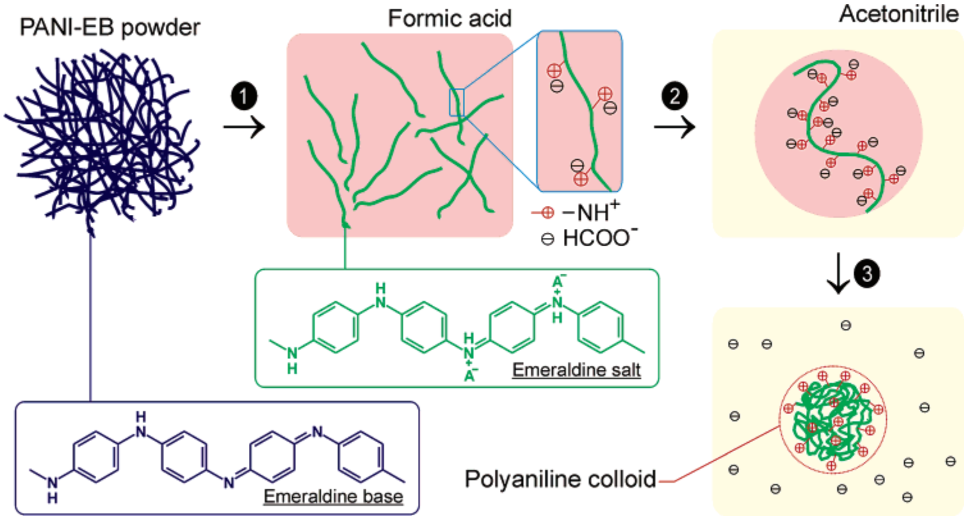

Figure 1. Formation of polyaniline colloids by dispersing polyaniline/formic acid solution into acetonitrile.

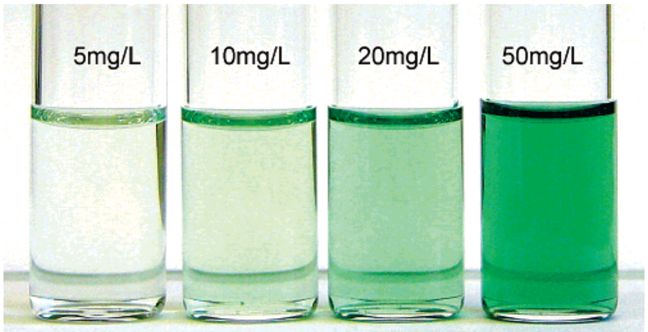

Figure 2. A photograph of a series of polyaniline colloidal suspensions with different concentrations.

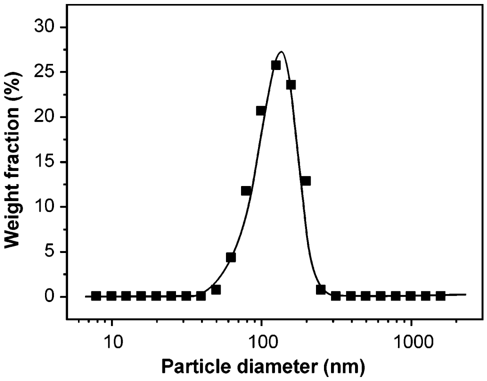

Figure 3. Particle size distribution of the 10 mg/L polyaniline colloidal suspension characterized by dynamic light scattering.

emeraldine base form of polyaniline has reasonable solubility in formic acid, which unravels the randomly entangled polymer chains and dissolves the polymer down to its chain level. Formic acid simultaneously protonates polyaniline at the amine sites on the polymer chain, converting it into the conducting form, polyaniline emeraldine salt. Second, although acetonitrile does not dissolve polyaniline, this nonaqueous solvent is miscible with formic acid. Consequently, the formic acid droplets dispersed in acetonitrile will shrink in size and eventually dissipate into the surrounding medium. As the formic acid droplets shrink in size, the polyaniline chains that are contained within them will be compressed and shaped into spherical particles. Meanwhile, the polyaniline emeraldine salt will start to dissociate into ions in the high dielectric constant medium presented by the acetonitrile. This will result in the formation of positively charged polyaniline colloids. Due to the electrostatic repulsion between these spheres, a stable polyaniline colloidal suspension can be attained. A photograph of polyaniline colloidal suspensions having varied concentrations is shown in Figure 2. The green color of the suspension indicates that the polyaniline colloids are indeed highly protonated. These suspensions are very stable with no visible sedimentation occurring after they are prepared. This suggests that the polyaniline emeraldine salt is sufficiently dissociated in acetonitrile, giving rise to adequate repulsive forces between the colloidal particles to maintain their state of suspension. The particle size distribution for the 10 mg/L polyaniline colloids, as characterized by dynamic light scattering, is shown in Figure 3. The average particle diameter was found to be 115.6 nm with a relatively narrow distribution (standard deviation = 55.4 nm). This particle size falls into the low end of the size range that has been previously reported for the polyaniline colloids obtained from dispersion polymerization.

The charge-stabilization mechanism that is depicted in Figure 1 can be potentially an approach for forming colloids of conducting polymers in general, because most known conducting polymers are ionic systems with cationic polymer backbones and compensating anionic dopants. In addition, the method of preparing polyaniline colloidal suspensions by dispersing polyaniline/formic acid solution into acetonitrile has the following advantages over dispersion polymerization: (1) The polyaniline colloids formed are entirely based on a charge-stabilization mechanism. This is fundamentally different from what is involved in a dispersion polymerization, in which the colloidal particles were protected from further aggregation by a surface layer of steric stabilizers. Without the presence of steric stabilizers, the colloids formed are purely polyaniline. Furthermore, the solvents involved in the formation of colloids, formic acid and acetonitrile, are both volatile and can be easily removed. Hence, the processibility of a “soluble” colloidal solution can be attained without introducing any additives that remain as impurities. (2) In a dispersion polymerization, the processes of polymerization and colloid-formation take place simultaneously. However, by starting with an already polymerized product, the two processes are now disengaged and

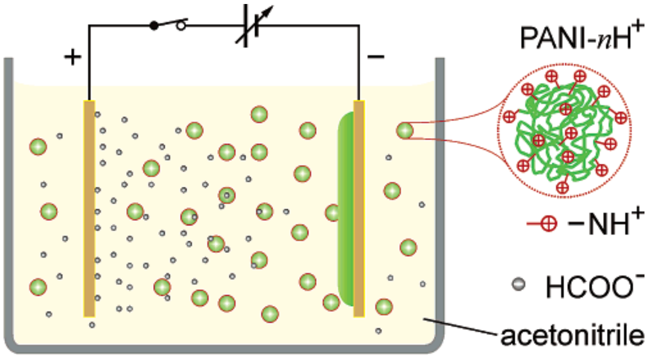

Figure 4. A schematic illustration of the setup used for the electrophoretic deposition of polyaniline from its colloidal suspension. A flat platinum foil was used as the counter electrode. A platinum-coated Si or ITO-coated glass substrate was used to collect polyaniline colloids. The size of the electrodes is 2.5 cm × 1.5 cm, the electrode separation is 4 mm, and the cell capacity is ~5 mL.

therefore better process-property control can be achieved. One of our ongoing studies is to explore the feasibility of adjusting the mean size and size distribution of the colloidal particles through controlling the molecular weight and weight distribution of the starting polyaniline.

B. Electrophoretic Deposition of Polyaniline. The electrophoretic deposition of polyaniline from its colloidal suspension is illustrated schematically in Figure 4. With an electric field applied, the positively charged polyaniline colloids are collected onto the electrode that has a negative bias, and, as a result, a thin film of polyaniline can be formed on the electrode surface. The deposition of polyaniline was confirmed by FTIR measurements. As shown in Figure 5A, the specular reflectance IR spectra measured from films deposited on platinum substrates reveal characteristic absorptions of polyaniline, for example, $\nu_{\mathrm{N-H}}$ at 3390 cm^{-1}, $\nu_{\mathrm{C-N}}$ at 1300 cm^{-1}, and ring stretching vibrations at 1515 and 1600 cm^{-1}.[40] Also note that the absorption peak at 1680 cm^{-1} originates from $\nu_{\mathrm{C=O}}$ of the residual formic acid. The gradual increase in absorbance over time clearly indicates that the film deposition can be well managed by controlling the duration of the deposition. The optical absorption spectra obtained from films deposited on ITO-coated glass substrates with different voltages applied for 60 s are shown in Figure 5B. The absorption bands at 420, 490, and 630 nm are due to the $\pi-\pi^*$ transition and the excitations associated with the polaronic sub-gap energy levels.[41] The increase in the overall peak intensities with applied voltage suggests that film deposition occurs at a faster rate when a higher voltage is applied. Obviously, the applied voltage has a significant impact on the mobility of the colloids. It is well established that the electrophoretic mobility of colloidal particles, μ, can be expressed as follows:[42]

$$\mu = \frac{\zeta \cdot \epsilon \cdot V}{4\pi \cdot \eta \cdot d}$$

where ζ is zeta potential, ϵ is the dielectric constant of the medium, V is the applied voltage, η is the viscosity of the suspension, and d is the electrode separation. Hence, modulating the applied voltage can be used to adjust the rate of deposition by influencing the electrophoretic mobility of polyaniline colloids. The voltage required to initiate the electrophoretic deposition was found to be relatively low. This is because the polyaniline colloids are highly solvated with a low density, and they have relatively high electrophoretic mobility in acetonitrile,

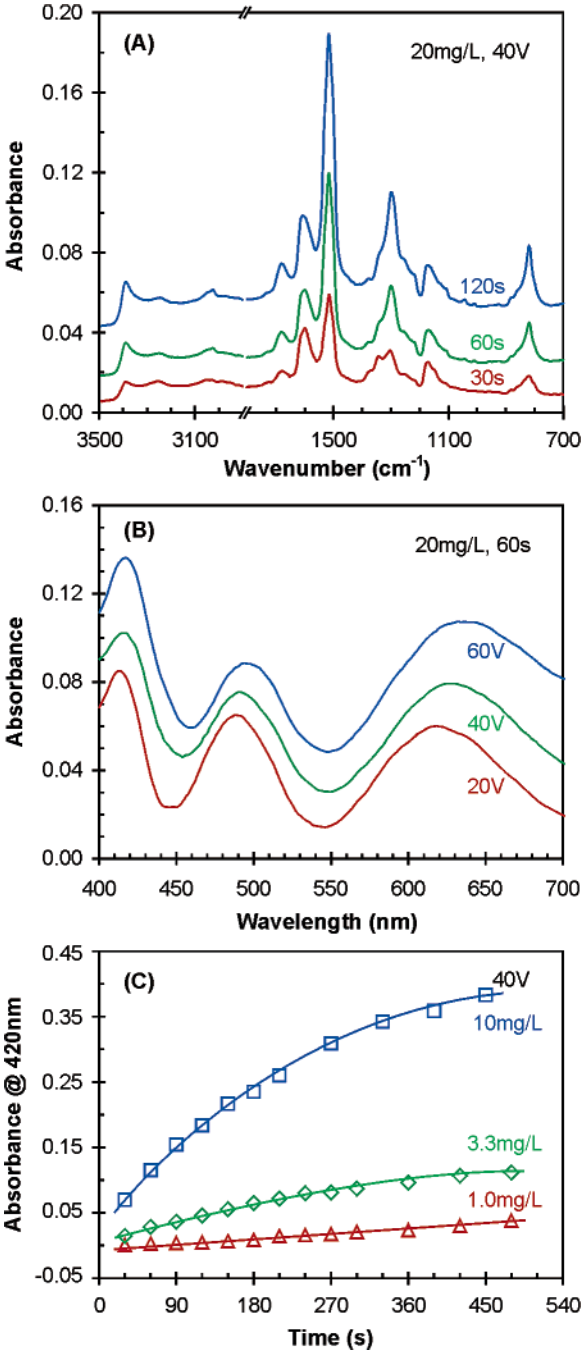

Figure 5. (A) Specular reflectance IR spectra of polyaniline films deposited on platinum-sputtered silicon substrates. The films were deposited at 40 V from 20 mg/L polyaniline colloidal suspension with different deposition times: 30, 60, and 120 s. The spectra have been offset for clarity. (B) Optical absorption spectra of films deposited on ITO-coated glass substrates. The deposition was carried out for 60 s from 20 mg/L suspension with different applied voltages: 20, 40, and 60 V. (C) Change in the optical absorbance at 420 nm versus deposition time for films prepared at 40 V from suspensions of different concentrations: 1.0, 3.3, and 10 mg/L.

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a medium with a high dielectric constant, and low viscosity. Furthermore, additional control can be achieved by limiting the concentration of the colloidal suspension. By following the optical absorbance at 420 nm, the deposition process can be closely monitored. The results in Figure 5C confirm that the rate of deposition can be effectively controlled by regulating the colloid's concentration. The deposition proceeds at a constant rate initially and then decelerates at later stages of the deposition as the colloidal particles are depleted within the cell. In brief, we have demonstrated that the collection of the polyaniline colloids can be well controlled with great flexibility through tuning a combination of process parameters including the duration of the deposition, the applied voltage, and the colloid concentration.

C. Electrophoretic Patterning of Polyaniline on Microfabricated Devices. As demonstrated in the previous section, the polyaniline colloidal suspensions have excellent processibility when applied electrophoretically. More significantly, the method provides the means for delivering controlled amounts of materials to desired locations by manipulating the electric field. This makes possible the patterning of polyaniline, a technique that could be attractive, particularly for practical device applications. For instance, in our studies, we have tried to incorporate polymeric materials onto a MEMS platform, the NIST microhotplate,[38,39] a conductometric gas sensor with an embedded microheater. In addition to its small size, the microhotplate has a rather complex layered structure that is shown in Figure 6. The plate is suspended over an etch pit with very brittle support beams. Surface contacts are isolated from the embedded polysilicon heater with only a thin layer (~500 nm) of SiO_2. In previous efforts, we attempted electrochemical deposition on these platforms without much success because the device could not withstand the highly acidic environment, a prerequisite for the electropolymerization of aniline. We have managed to deliver small volumes of polymer solution onto individual microhotplates by using a small diameter capillary, but this method provides little control over the film deposition process due to the difficulties in manipulation.

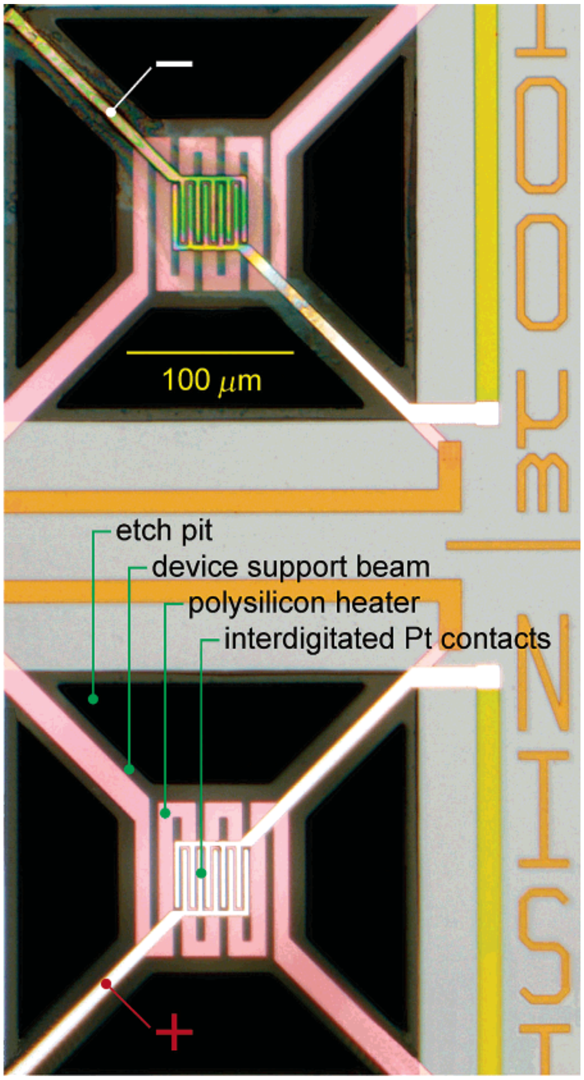

Figure 6. Electrophoretic patterning of polyaniline on a NIST microhotplate sensor array. The image shows a half section of a 4-element sensor array with polyaniline electrophoretically deposited on the upper sensing element. The electrophoretic deposition was carried out in 10 mg/L polyaniline colloidal suspension with 4 V applied for 120 s.

To demonstrate the versatility of the electrophoretic technique, we deposited polyaniline from its colloidal suspension onto an individual sensing element within a 4-element microhotplate sensor array. The packaged device was encapsulated with an insulating epoxy to electrically isolate the wirebonds and bonding pads prior to use. A small plastic bottomless cuvette was placed on the device, sealed with melt wax, and then filled with ~0.5 mL of 10 mg/L polyaniline colloidal suspension. As illustrated in Figure 6, the microhotplate to be coated with polyaniline has its surface contact biased with a negative voltage against the contact on an adjacent microhotplate that is used as the counter electrode. Only one set of digits from each of the interdigitated pair (the ones that are furthest apart from one another, labeled with "−" and "+" in Figure 6) was chosen so that the electric field will be strongest at the plate area. The use of existing surface contacts on the device for applying the electric field is not only a convenient choice, but it also offers the benefit of having a well-defined electrode separation, avoiding the complication of carefully positioning an external counter electrode. Because the anode−cathode separation is rather small (the adjacent microhotplates are separated by ~400 μm), a much lower voltage is required to generate the same field strength as compared to the type of macroscopic configuration schematically depicted in Figure 4. The result of the electrophoretic deposition carried out at 4 V from 10 mg/L polyaniline colloidal suspension for 120 s is shown in Figure 6. A thin film of polyaniline can be easily identified by its green color. The film has excellent coverage on the plate area. Deposition also occurred on the device support beam, due to the exposed platinum there. This is merely an aesthetic nuisance and should not affect device performance. What is significant is that no deposition was observed on the other three microhotplates of the 4-element sensor array, suggesting that the electrophoretic deposition is indeed a practical method for patterning polyaniline on miniaturized devices. Even though it contains a small fraction of formic acid, the polyaniline colloidal suspension is only mildly acidic. For example, for the 10 mg/L polyaniline colloidal suspension that has 1% of formic acid in acetonitrile by volume, the pH was measured to be 2.38. Because of the noncorrosive nature of the polyaniline colloidal suspension and a low voltage that is necessary to drive the polyaniline colloids, the electrophoretic deposition process does not appear

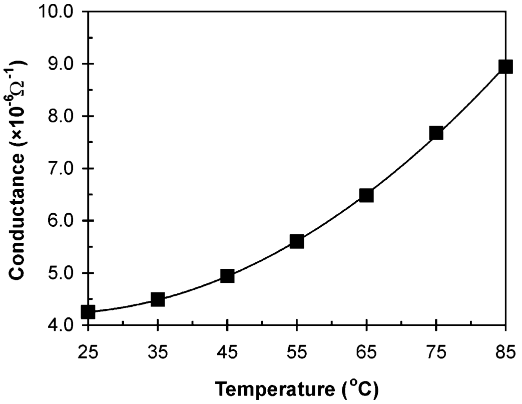

Figure 7. Temperature dependence of the conductance of an electrophoretically deposited polyaniline film measured on a microhotplate.

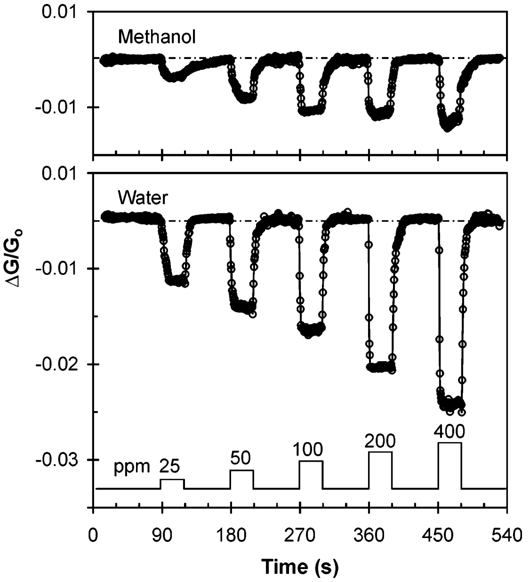

Figure 8. Relative changes in the conductance of an electrophoretically deposited polyaniline film upon exposure to various concentrations of methanol and water vapors in dry air at room temperature.

to undermine the device integrity. After the electrophoretic deposition process, the embedded polysilicon microheater remains functional and the temperature dependence of the electrophoretically patterned polyaniline can be well characterized; these results are shown in Figure 7. The enhancement of film conductance at higher temperatures can be attributed to the thermal excitation of electrons, which leads to an increase of the carrier density in the semiconducting polyaniline. This phenomenon has been previously investigated, and the details were described elsewhere.[43]

The sensitivity of the microhotplate device with an electrophoretically integrated polyaniline film was also evaluated. Figure 8 shows the relative changes of film conductance in response to ppm levels of methanol and water vapors in a dry air background. In both cases, the sensor signal magnitude correlates well with the gas concentration, with relatively short response and recovery times. For example, the response time characterized by $t_{1/2}$, the time that is required for sensor signal to reach 50% of the maximum signal, is around 3 s for the 100 ppm water exposure. While only room temperature data are shown here, we note that the effect of temperature on the sensor response can be conveniently probed with the microhotplate platform.[43]

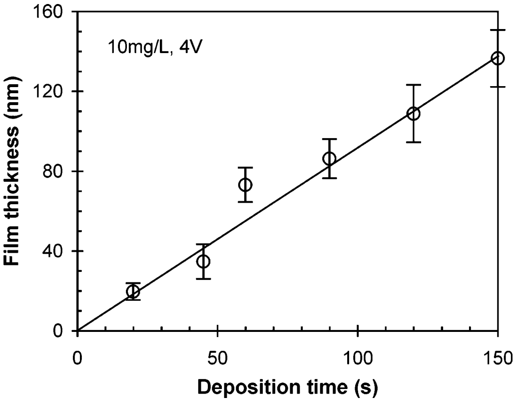

Figure 9. The thickness of electrophoretically deposited polyaniline films on "dummy" microhotplates as a function of the deposition time. The deposition was performed at 4 V from 10 mg/L polyaniline colloidal suspension.

To determine the film thickness, the electrophoretic deposition was also carried out on the so-called "dummy" microhotplates. These are devices that have similar geometry and surface characteristics but no heater or etch pit, so that it is possible to use a profilometer to get a direct measurement of the thickness for a deposited film. Figure 9 shows the film thickness as a function of the deposition time, from which a linear correlation can be established. The linear correlation occurs because the colloid concentration was relatively constant throughout the whole deposition process: considering the microscopic size of the electrodes, the consumption of the colloidal particles from the suspension is negligible. The rate of deposition determined from the graph is roughly 0.91 nm/s. An interesting observation is that the film thickness measured in a dried state by profilometer at early stages of the deposition is much lower than the average particle size that is characterized by light scattering. This suggests that (1) the polyaniline particles are considerably swollen in a liquid medium, and (2) they are soft-core colloids, which collapse upon impact when electrophoretically driven onto the collecting electrodes. The discrepancy can also be partially attributed to the fact that, due to factors such as irregularity (i.e., not strictly spherical) in particle shape together with Brownian movements of the particles, the average size that is determined by a scattering method is typically larger than their true average.

D. Morphology of the Electrophoretically Deposited Polyaniline. The film deposition process was also characterized by a series of SEM images recorded after different deposition times. The interdigitated electrodes are separated by 2 μm as shown in Figure 10a. At 20 s, the electrodes were not fully covered, but a fair amount of the polymer was observed on the insulating surface between the platinum digits. By having the opposing electrodes on the same planar surface when the electrophoretic deposition was carried out on the device, the direction of the electric field is nearly parallel to the surface plane of the interdigitated electrodes. This substantially minimizes the variation in field strength between the platinum digits and interdigit space, leading to a more evenly distributed electric field on the plate area. That effect becomes more evident in the image that is recorded at 45 s: both the metal digits and the

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(43) Li, G.; Josowicz, M.; Janata, J.; Semancik, S. *Appl. Phys. Lett.* **2004**, *85*, 1187−1189.

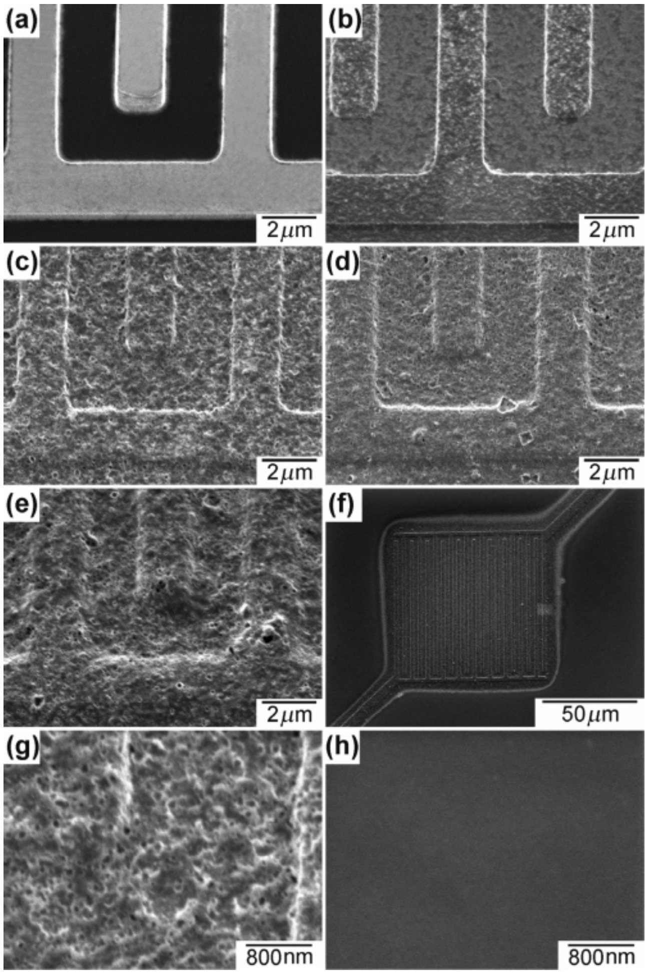

Figure 10. SEM images of the films electrophoretically deposited on "dummy" microhotplates from 10 mg/L polyaniline colloidal suspension at 4 V after (a) 0 s, (b) 20 s, (c) 45 s, (d) 90 s, and (e) 150 s. (f) An overview of the device after electrophoretic deposition. (g) A close-up of the electrophoretically deposited polyaniline film. (h) An SEM image of the film spun cast from polyaniline/formic acid solution.

insulating interdigit SiO_2 surface are now fully covered (Figure 10c). Once a thin layer of polyaniline is in place, the film itself serves as an "electrode" that promotes further deposition. These observations are important because microfabricated devices often have a hybrid surface that is composed of well-patterned metals and SiO_2. Under many circumstances, the full coverage of the device surface is critical for realizing proper device functionality. The SEM results in Figure 10 demonstrate that electrophoretic deposition adapts to such device configurations better than other comparable techniques. Consider electrochemical deposition/polymerization as an example; although it has a somewhat similar setup involving applied potential biases, the oxidation of aniline monomers and succeeding polymerization/deposition strictly happen on the surface of the metal electrodes. Because the starting building blocks are aniline molecules, it would be rather difficult to span the growth of polyaniline over a micrometer-scale separation.[44] Also, keep in mind that carrying out redox reactions in an acid aqueous medium poses great threats to device integrity. In other words, such a microfabricated device is not the ideal platform for carrying out electrochemical reactions. In contrast, there are no redox reactions of aniline or polyaniline involved in an electrophoretic process. Even though an electric field originates from and terminates on conducting electrodes, it can be easily projected onto insulating surfaces. Because the building blocks for film formation are colloids of polyaniline over 100 nm in size, it would be much easier to close a micrometer-scale gap.

As the deposition progresses (Figure 10d,e), further increases in the film thickness and improvement in the film coverage are apparent. An image of the whole device shown in Figure 10f clearly indicates that the deposition is quite localized. A close-up (Figure 10g) of the electrophoretically deposited polyaniline film reveals that it has a rough surface and a fairly porous structure, with pore size around 100 nm. In comparison, a film that has been spun-cast from polyaniline/formic acid solution (Figure 10h) has a very smooth and compact structure. The surface uniformity can be improved by downsizing the particle size or further homogenizing the electric field distribution. As mentioned earlier, one of our studies in progress is to correlate the molecular weight of polyaniline to the size of the polyaniline colloids, and to examine how the molecular weight of the starting material would affect the film microstructure. To improve field uniformity, approaches similar to electrospinning can be utilized by positioning an external microelectrode as the counter electrode and then carrying out the electrophoretic deposition while rotating the device. Note that a nanoporous film with a rough surface may not be ideal for certain application; however, it is in fact beneficial for gas sensing due to the increased surface area and improved gas diffusion. This explains the relatively short response and purge times observed in the sensing data shown in Figure 8.

IV. Conclusion

In summary, we have presented a convenient approach for forming polyaniline colloids with a size of ∼100 nm. It was demonstrated that the polyaniline colloidal suspensions have excellent processibility when applied electrophoretically. The electrophoretic deposition of polyaniline colloids can be controlled with great flexibility by adjusting various process parameters such as the duration of the deposition, the colloid concentration, or the applied voltage. In addition, the electrophoretic patterning of polyaniline from its colloidal suspension was proven to be a scalable technique: it can be applied to macroscopic substrates as well as microfabricated device features.

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Supporting Information Available: A video showing the electrophoretic deposition of polyaniline on a NIST microhotplate. This material is available free of charge via the Internet at http://pubs.acs.org.

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(44) Li, G.; Josowicz, M.; Janata, J. *Electrochem. Solid-State Lett.* **2002**, *5*, D5−D8.