Versatile solution for growing thin films of conducting polymers


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The method employed for depositing nanostructures of conducting polymers dictates potential uses in a variety of applications such as organic solar cells, light-emitting diodes, electrochromics, and sensors. A simple and scalable film fabrication technique that allows reproducible control of thickness, and morphological homogeneity at the nanoscale, is an attractive option for industrial applications. Here we demonstrate that under the proper conditions of volume, doping, and polymer concentration, films consisting of monolayers of conducting polymer nanofibers such as polyaniline, polythiophene, and poly(3-hexylthiophene) can be produced in a matter of seconds. A thermodynamically driven solution-based process leads to the growth of transparent thin films of interfacially adsorbed nanofibers. High quality transparent thin films are deposited at ambient conditions on virtually any substrate. This inexpensive process uses solutions that are recyclable and affords a new technique in the field of conducting polymers for coating large substrate areas.

Marangoni | surface tension | thin film technology | organic electronics

Conducting polymers hold promise as flexible, inexpensive materials for use in electronic applications including solar cells, light-emitting diodes, and chemiresistor-type sensors (1–3). Whereas traditional nonconjugated polymers are often solution-processable, many organic conducting polymers have been notoriously difficult to process into films. Thin films of conducting polymers offer a large ratio of charge carriers to volume of active layer (4) and can achieve high field-effect mobilities as a result of low-dimensional transport (5). Therefore a simple, scalable, cost-effective deposition technique for conducting polymers that produces a uniform thin film morphology reproducibly is needed.

Film-forming methods for conducting polymers on the basis of solution processing, electrochemistry, and thermal annealing have been reported in the literature but suffer from a variety of problems. The conducting polymers polyaniline (PANi), polythiophene, and their derivatives such as poly(3-hexylthiophene) (P3HT) are commonly processed into nanoscale thin films via spin coating (1, 5–7) for applications in organic photovoltaics, thin film transistors, and electrochemical devices (8–12). However, spin coating is a technique that suffers from a low material utilization yield and is therefore not cost-effective (11), a fact that hinders its potential for scale-up. Another well known deposition strategy is the electrochemical growth of conducting polymer thin films via galvanostatic, potentiostatic, or voltammetric routes (9, 13–15). An inherent limitation of using electricity for thin film deposition is the dual role played by the electrode/substrate, which excludes the possibility of film deposition on a nonconducting substrate. This problem also applies to electrospraying because it requires a high voltage across electrodes (11). Other solution-based methods also present challenges; for example, the Langmuir–Blodgett technique produces films of P3HT that suffer from aggregation and poor adhesion to a substrate during vertical deposition and can require hours for the fabrication of a single film (16). Thermal evaporation can cause deformation of a substrate due to gradients in temperature during deposition; this method also requires high vacuum and/or high temperature equipment (11). Hard templates can improve order in film morphology but are difficult to remove (12, 13). Another method called in situ polymerization can lead to nanoscale order in a transparent polyaniline film but requires 24 h at 5 °C for deposition of a single layer (17). Dip coating uses large amounts of material and often suffers from uneven drying (8, 18). Despite the litany of reported methods including electrostatic adsorption (19), drop casting (20, 21), grafting (22), slide coating (23), and ink-jet printing (4), their limitations range from reproducibility issues and cost effectiveness to lack of scalability. Therefore, a universal solution is needed that reliably deposits any conducting polymer film on any substrate.

Here we demonstrate a solution-based method for growing transparent thin films of nanofibers of polyaniline, polythiophene, and poly(3-hexylthiophene) on virtually any substrate under ambient conditions. Emulsification of two immiscible liquids and polymer nanofibers leads to an interfacial surface tension gradient, viscous flow, and film spreading. Surface tension gradients have previously been used to form inorganic nanoparticle films (24–27). The films created here are of organic conductors and possess nanoscale order characterized by monolayers of nanofibers. This film growing technique for conducting polymers can be readily scaled up and the solutions recycled. Morphological homogeneity, reproducible thickness control, and the simplicity of this film-making method hold promise for future device fabrication.

This study began when an interesting phenomenon was observed—while purifying an aqueous dispersion of polyaniline nanofibers by liquid extraction with chloroform, a transparent film of polymer spread up the walls of a separatory funnel. Shaking the solvent mixture removed the film, but left standing, the film rapidly reformed. Here we develop this phenomenon into a solution-based method to grow films of nanostructured conducting polymers that could facilitate their use in applications ranging from actuators to sensors (28). The vigorous agitation of water and a dense oil such as chlorobenzene leads to the formation of water droplets dispersed in an oil phase. The water–oil interface of the droplets serves as an adsorption site for surface active species such as surfactants and solid particles. The interfacial tension is lowered proportionately to the surface concentration of the adsorbed species, and when their concentration is

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distributed unevenly, an interfacial surface tension gradient develops, which in turn causes fluid films to spread over solid surfaces in what is known as the Marangoni effect. This type of directional fluid flow is found in the self-protection mechanisms of living organisms (29) and can be exploited for use in lubrication (30), microfluidics (31), lab-on-a-chip (32), and potentially high-density data storage (33).

**Results and Discussion**

A highly transparent, homogeneous thin film of polymer nanofibers can be grown on virtually any substrate by vigorously mixing water, a dense oil, and polymer nanofibers (Fig. 1). This emulsification process is partly responsible for film growth. Agitation leads to water coating the hydrophilic walls of the container and to aqueous droplets becoming dispersed in the oil phase (Fig. 1, A, D, and E). Solid particles such as nanofibers can serve as a stabilizer in what is referred to as a Pickering emulsion by lowering the interfacial surface tension between immiscible liquids (34). Mixing provides the mechanical energy required for solvating the polymer nanofibers in both liquids, thus trapping the nanofibers at the water–oil interface via an adsorption process that is essentially irreversible (24–27). Theoretical studies have determined that the energy required for removing adsorbed particles from any interface is much greater than the energy required for spreading (35). Therefore, if nanofibers are trapped at an interface and experience a gradient in surface energy, spreading occurs. When agitation is stopped, the input of mechanical energy subsides, allowing the water droplets to rise to the top of the oil layer and coalesce. The total interfacial surface area decreases during coalescence, expelling oil and nanofibers out from the droplets, producing a spontaneous concentration gradient of irreversibly adsorbed nanofibers, and thus creating a Marangoni pressure at the water–oil interface (24–27, 35). An interfacial surface tension gradient arises that pulls expelled nanofibers into areas of higher interfacial surface tension, while a film of nanofibers spreads up and down the container walls as a monolayer squeezed between water and oil (Fig. 1 B and F–H). Note that there is no film growth on the glass walls that surround the bulk water phase because a water–oil interface is not present (Fig. 1 C and I). A video is available along with this manuscript demonstrating the film growth of a polyaniline nanofiber film (Movie S1).

During film growth, the water layer assumes the shape of a catenoid with an inner oil channel containing the majority of the nanofibers. Water minimizes its surface free energy by adopting this shape (36). Viscous flow inside the catenoid creates fluid movement both up and down from the thinnest toward the thickest section of the channel (37). Coalescence thins out the inner channel (Fig. 1 F–H) and eventually leads to the catenoid breaking up, terminating viscous flow. Two distinct bulk phases are established, causing the redistribution of nanofibers (Fig. 1 C and I). Water–oil interfaces containing nanofibers are found both adjacent to air and below the bulk water layer. The top interface contains a concentration gradient of nanofibers that continues to drive film growth upward for a few seconds after the catenoid breaks up. This concentration is exploited to fully coat a glass slide as it is pulled out of the solution. The bottom interface contains a polymer reservoir of nanofibers that can be used for the growth of additional films.

Polyaniline nanofiber films were grown on glass slides (see SI Materials and Methods) by using different binary mixtures of water and dense halogenated solvents to determine the optimal experimental conditions for film growth. The maximum attainable spreading height was compared against the interfacial surface tension of the binary immiscible mixture used for growing each film. The results indicate that the greater the interfacial tension, the higher the climbing height for an upward spreading film and that the interfacial surface tension controls nanoscale morphology (SI Text and Fig. S1 A and B). A greater interfacial surface tension pulls on the nanofibers with a stronger force than a lesser one and allows a film to climb up the substrate against gravity, leading to greater spreading heights. Nanofiber films climbed highest when water and carbon tetrachloride (interfacial surface tension of 45 dyn/cm) were used, followed by water and chloroform (32.8 dyn/cm), and last by water and methylene chloride (28.3 dyn/cm). Film growth is driven by minimization of the total interfacial surface free energy of the system (38).

The interfacial surface area between immiscible liquids varies proportionally with the diameter of the container, and to understand its effect on film growth containers of different aspect ratios were tested. The speeds and climbing heights of films were measured in containers with an aspect ratio of 2 (wide diameter container) and 3.3 (narrow diameter container). A speed of ~1 cm/s is achieved by using containers with an aspect ratio of 2; this relatively fast speed can be explained by the large number of droplets and highly energetic coalescence that is observed during film growth. Controlling the interfacial surface area by the aspect ratio of a container also controls film morphology (Fig. S1 C and D). Although fast film production may be convenient, using a wide diameter container for growing a film has a major drawback—the climbing height and surface coverage of the film is typically about 20% less than in a film grown in a narrow diameter container.

Transparent thin films of conducting polymer nanofibers can be fabricated in a palette of colors as displayed by the films of polyaniline and polystyrene in Fig. 2A; pictured, from left to right, are red chloride doped polystyrene, green perchloric...
acid doped polyaniline, and blue dedoped polyaniline. These polyaniline films were grown by using an aqueous dispersion of para-toluene sulfonic acid (p-TSA) doped nanofibers and chloroform. The films were then exposed to either base or acid vapors in order to dedope (blue) or further dope (green) them, respectively. Note that a p-TSA doped polyaniline film has a greater than 70% light transmittance as demonstrated by the clearly observable University of California Los Angeles logo placed behind the slides.

Scalability is demonstrated in Fig. 2B by the growth of a homogeneous transparent p-TSA doped polyaniline nanofiber film deposited on a large glass substrate (12.7 × 17.7 cm). This process is accomplished in seconds by using 8 mL of an aqueous polyaniline nanofiber dispersion [4 g/L], an inexpensive rectangular plastic container, and the solvents: recycled chlorobenzene and water. This immiscible binary system establishes a liquid–liquid boundary of sufficient interfacial surface energy on a hydrophilic solid surface to produce film spreading. Thus the selective deposition of a film occurs on glass when polymer nanofibers and the solvent mixture are housed in a hydrophobic container.

The coated film surface area as a function of the polymer concentration was studied by varying the amount of solids present at the liquid–liquid interface during film growth. A series of films were deposited on microscope glass slides by using 3 mL of deionized (DI) water, 6 mL of chlorobenzene, and a 4 g/L aqueous dispersion of p-TSA partially doped polyaniline nanofibers. Once dried, the surface area of each film was measured by using a grid that served as a background in order to accurately count square segments. As the concentration of polymer in solution increased, so did the surface area of the coating (Table S1). Approximately 99% of the surface area of a 1.875 mm² substrate was coated by using 0.16 mL of the polymer dispersion, i.e., 0.64 mg of solids.

A homogeneous solid-state film can be deposited onto a nonactivated hydrophobic surface using a binary system containing water and a fluorocarbon that behaves like liquid Teflon® possessing extremely low wettability and surface energy (39, 40). This binary immiscible system is comprised of solvents that represent end-of-the-spectrum polarities, possess a large interfacial surface tension, and lead to selective wetting as the nonpolar fluoroalkane deposits a self-adsorbed solid monolayer on the surface of the hydrophobic substrate (41, 42). Vigorous mixing of this nonpolar perfluorinated fluid with water leads to an emulsion of droplets stabilized by a significant negative charge (43), trapping nanofibers at the liquid–liquid interface, thus allowing droplet coalescence to deposit a film. A perfluorinated fluid is chemically inert, shows excellent toxicological properties, and evaporates cleanly from a surface (44). Films produced by drying under ambient conditions are homogeneous and conductively continuous.

Deposition on nonactivated hydrophobic surfaces is demonstrated in Fig. 2C (see SI Text, SI Materials and Methods, and Fig. S2). A transparent film of perchloric acid doped polyaniline nanofibers was deposited on an oriented polyester substrate (10.2 cm × 8.4 cm × 0.0254 cm); it was coated via directional fluid flow, by using 6 mL of an aqueous polymer dispersion [4 g/L], 3 mL of water, and 60 mL of a perfluorinated fluid such as Fluorinert FC-40®. All chemicals were combined and vigorously agitated in a 250 mL wide-mouth glass jar, and a clean hydrophobic substrate was then introduced into the glass jar’s liquid–liquid interface. This setup was then vigorously agitated and a green film immediately deposited on the plastic substrate. The coated green colored substrate was removed after 1 min of
agitation, washed with water, and allowed to dry under ambient conditions producing a conductively continuous film.

Molecular interactions between the free surface energy of interfacially adsorbed nanofibers and the substrate can dictate film morphology (45). Perchloric acid doped polyaniline forms a film with an average thickness of a single nanofiber, as can be seen in Fig. 2 D–F. This morphology occurs because the nanofibers are interfacially extruded when sandwiched between a layer of oil and a layer of water as demonstrated in Fig. 2E, which shows a close-up image of a single monolayer of nanofibers. Single monolayers of polyaniline nanofibers can also be deposited by using dopants such as camphorsulfonic acid or p-TSA. Films possess conductivities of up to 3 S/cm and can be patterned by using a polydimethylsiloxane stamp (see SI Text and Figs. S3 and S4).

The level of adhesion between a conducting polymer coating and a solid surface was studied by systematically depositing polyaniline nanofiber films on substrates with different surface energies. Glass, for example, was first immersed in concentrated nitric acid for 48 h, rinsed in water, dried, and cleaned by using an oxygen plasma before film deposition. In order to test the strength of adhesion between a film and substrate, a peeling test was performed by pressing an adhesive tape onto a dry film and pulling at a 90° angle from the surface. Table S2 shows the peeling data collected from films dried at 25 °C and 55 °C for 5 d; the number of peels is defined by how many times the test was carried out in order to completely remove the film from a substrate. The results indicate that the strength of adhesion increases with annealing temperature and soda glass possesses the greatest adhesion strength, requiring 10 peels to completely remove the film, whereas borosilicate glass, quartz, indium tin oxide (ITO), mica, and aluminum foil were removed with 7 peels.

Poly(3-hexylthiophene) is a particularly useful solution processed semiconducting polymer, because it offers a high field-effect mobility in organic field-effect transistors (18, 23) and benefits from absorption in the visible solar spectrum as a donor material in organic solar cells (12). Thin films of poly(3-hexylthiophene) are employed in the fabrication of electronic devices such as photodetector chemical cells (15), textured photo voltaics, and nanorod solar cells (9, 12). The morphology of a thin film of P3HT in an organic field-effect transistor alters the charge injection mechanism that determines whether current-voltage behavior is linear (ohmic) or nonlinear (21) and is also critical to device efficiency because the solid–solid interface between a P3HT film and an oxide layer confines field-induced carriers (18).

Poly(3-hexylthiophene) nanofibers (Fig. 2 G–I and Fig. S5) were synthesized by using an initiator-assisted polymerization protocol reported to yield bulk quantities of conducting polymer nanofibers such as polyaniline, polypyrrole, polyanthiphene, and their derivatives (13). The deposition of a thin film of P3HT nanowires is attractive because 1D nanostructures have high mechanical flexibility (13) and afford large surface to volume ratios (15), as well as enhance charge percolation and device efficiencies by increasing the donor–acceptor interfacial area (9, 12) and π–π stacking in a photovoltaic bulk heterojunction (5). A thin P3HT nanofiber film was deposited on a hydrophilic glass substrate by using hexane and a 1:1 mixture of nitromethane to acetonitrile. The nanoscale solid-state morphology of this film is highly homogeneous as demonstrated by SEM, and it is comprised of a single nanofiber monolayer with an atomic force microscopy (AFM) height profile of 75 nm in thickness (Fig. 2 G–I).

A film of commercial poly(3-hexylthiophene) was deposited on a nonactivated hydrophobic self-adsorbed monolayer (SAM) of octadecyltrichlorosilane on a surface of SiO2, by using chlorobenzene and Fluorinert FC-40®, which affords a simple and scalable technique for the fabrication of an organic field-effect transistor (see Fig. 3 A–C). This device was fabricated by conventional photolithography, comprised of gold bottom contacts for low-cost manufacturing (4) and modified SiO2 separation channels (46).

The organic SAM covers the device’s separation channels with a C18 hydrocarbon chain monolayer, alters the surface energy of SiO2, and renders the substrate hydrophobic. A high gate dielectric such as this octadecyltrichlorosilane self-adsorbed monolayer works as a buffer that prevents the trapping of charge carriers at the dielectric-semiconductor interface (3) and provides low leakage current (47) and higher field-effect transistor mobilities (6). This device exhibited a mobility of 2.7 × 10−3 cm²/V s with an on/off ratio of 1,000; the schematic flow process diagram and electrode geometry are shown in Fig. S6.

As a proof of concept, a hybrid film was grown on SiO2 by using single-walled carbon nanotubes and polyaniline nanofibers. These water dispersible carbon nanostructures offer the potential to enhance electronic properties of films. Aligned carbon nanotube ropes wrap themselves around a single nanofiber (Fig. 3F) and link multiple nanofibers together (Fig. 3G). The electrochemical behavior of polyaniline nanofiber films is characterized (see SI Materials and Methods) by probing the oxidation states of the polymer by using cyclic voltammetry (CV). Transitions from leucoemeraldine to emeraldine and from emeraldine to pernigraniline are assigned as shown in Fig. 4. Hydrochloric acid, perchloric acid, and para-toluene sulfonic acid doped polyaniline films all show their first oxidation peak at 0.25 V, a leucoemeraldine to emeraldine transition. The second oxidation peak at 0.95 V is because of the transition from the emeraldine to the pernigraniline form. In the p-TSA doped polyaniline nanofiber film, the oxidation processes show an increase in current for the first oxidation peak, possibly because of traces of the chemical initiator employed in the synthesis of these nanofibers. An aromatic additive such as N-phenyl-1,4-phenylenediamine leads to a fast rate of increase in the first oxidation peak during a potential sweep (48). These cyclic voltammograms indicate that the polyaniline nanofibers as synthesized are in an emeraldine oxidation state (10, 49). These nanofiber films are transparent, robust, and capable of handling multiple cycles of CV. Only the area of the electrode immersed in the electrolyte changes color as the direction of the potential is switched.

The transparency of the film grown on ITO is demonstrated by how clearly the structure of polyaniline can be seen through the film. The nanofibrillar density of the films produced by Marangoni flow can be controlled by sequential deposition of layers of doped polyaniline nanofiber films (Fig. S4A). UV-visible (UV-vis) spectra show that every new layer produces an optical density of approximately 0.2 absorbance units. Each layer of film was allowed to dry for 30 min at ambient conditions before collecting a spectrum. The UV-vis absorption of polystyrene (Fig. 5B) obtained for a film sampled at different heights shows the expected absorption peaks (50). Deposition film mass can be controlled by the angle at which the film is grown because the mass of polymer deposited varies inversely with film height. Therefore, the optical density decreases as the film climbs up the substrate. This technique demonstrates the ability to control the film morphology via a concentration gradient (38). In addition, varying polymer concentration in the film growth solution changes surface packing of the nanofibers, enabling another method for controlling film morphology (see SI Text and Fig. S7).

In conclusion, the method described herein affords a simple and inexpensive solution for the growth of transparent thin films of conducting polymer nanofibers. Building on the concept that a fluid of lower surface tension (oil) will always spread over a fluid of higher surface tension (water) (51), we have demonstrated how an oil film can effectively carry dispersed organic nanostructures across an aqueous layer present on the surface of glass. Films rapidly deposit at ambient conditions within seconds and dry in minutes, and the solvents can be recycled. Large substrate areas can be homogeneously and reproducibly coated with high quality
Fig. 3. Film deposition for electronic devices. (A)–(C) A P3HT field-effect transistor and its output characteristic curve. (A) Close-up photographs of bottom-contact gold electrodes (yellow) and SiO$_2$ separation channels (blue). (B) SEM image shows a thin film of commercial P3HT deposited on SiO$_2$. (Scale bar: 3 μm.) (C) I-V curve of device exhibits a mobility of $2.7 \times 10^{-3}$ cm$^2$/V s with an on/off ratio of 1,000. (D)–(G) SEM images of PANi-SWCNT hybrid films on SiO$_2$. (D and E) The sequence shows dense coverage of SWCNT ropes that flow and envelop polyaniline nanofibers. [Scale bar: (D) 500 nm; (E) 200 nm.] (F) Single nanofiber wrapped by SWCNT ropes. (Scale bar: 100 nm.) (G) Transparent SWCNT ropes connect nanofibers together. (Scale bar: 200 nm.)

Fig. 4. Redox switching between oxidation states in polyaniline. The green emeraldine form of a polyaniline nanofiber film is dipped halfway into an electrolyte and electrochemically reduced to (A) transparent leucoemeraldine and then oxidized to (B) violet pernigraniline. An electrochromic transition is readily apparent as a polyaniline nanofiber film is cycled between reduced and oxidized forms. (C) The graph displays CV curves of polyaniline nanofibers doped with hydrochloric acid (HCl), perchloric acid (HClO$_4$), and p-TSA.

Fig. 5. Control over the density of deposited nanofibers during film formation can be monitored by UV-vis spectroscopy. (A) Each of the four layers of a p-TSA doped polyaniline nanofiber film grown on glass can be observed through their incremental increase (~0.2 units) in absorption. (B) A series of spectra collected at different heights along a polythiophene nanofiber film grown at a 60° angle demonstrates that optical density can be controlled by the angle of film growth. (Inset) A polythiophene nanofiber film grown at a 60° angle on a plastic substrate, ITO-polyethylene terephthalate, is flexible as shown by applying light pressure with blue gloved fingertips.
thin films. In addition, hydrophobic surfaces can be used as substrates for film growth by first activating the surface by using an argon–oxygen plasma or by simply growing directly on nonactivated hydrophobic surfaces.

**Materials and Methods**

**Polythiophene Nanofiber Synthesis.** Nanofibers were synthesized as previously reported in the literature (52). Typically, FeCl$_3$ (0.333 g, 2.1 × 10$^{-3}$ mol) was dissolved in 10 mL of acetonitrile, and thiophene (0.133 mL, 1.74 × 10$^{-5}$ mol) and terthiophene (0.0065 g, 2.61 × 10$^{-5}$ mol) were combined and dissolved in 10 mL of 1,2-dichlorobenzene. The amine mixture and the oxidant solution were then combined and mixed for 10 s and allowed to stand undisturbed for 7 d.


**Polythiophene Nanofiber Film Growth.** A binary insoluble solution comprised of a smaller aqueous phase and a larger organic layer was employed; this asymmetrical volume distribution leads to Marangoni flow (30). Typically, a glass slide can be coated with polythiophene when 1 mL of a nanofiber dispersion in acetonitrile (2 g/L) is mixed with 0.6 mL of DI water and 10 mL of chlorobenzene.

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