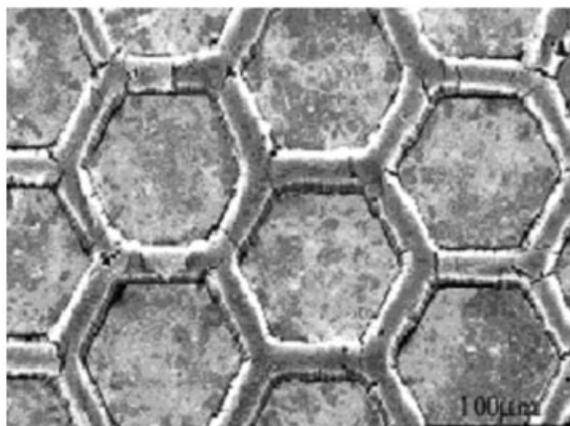


Summary: Owing to their π -electron delocalization along the backbone, conjugated polymers possess unique optoelectronic properties attractive for a wide range of applications in various electronic and photonic devices. Having a conjugated all-carbon structure with specific molecular symmetries, carbon nanotubes have also attracted a great deal of interest for optoelectronic applications. It is well known that surface and/or interfacial properties are of paramount importance for most optoelectronic applications. Recent developments in the field have clearly indicated the possibility of using radio-frequency glow-discharge plasma for introducing functional surfaces/interfaces with region-specific characteristics necessary for advanced electronic and/or photonic devices. In this article, we summarize our work on the use of plasma processes (both plasma treatment and plasma polymerization) for the surface and interface control of optoelectronic polymers and carbon nanotubes for potential applications in electronic and photonic devices, and reference is also made to other complementary work as appropriate.



A low magnification SEM micrograph of multicomponent, interposed, carbon nanotube micropatterns with non-aligned carbon nanotubes region-specifically adsorbed between aligned carbon nanotube patterns.

Controlled Surface Engineering and Device Fabrication of Optoelectronic Polymers and Carbon Nanotubes by Plasma Processes

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Introduction

Polymers offer many advantages over inorganic materials for applications in various electronic and photonic devices, including their versatility for fabrication (especially over a large area), flexibility, and low cost. Hence, polymers have traditionally been used as passivation and insulating materials in electronic packaging, lithographic resists, and inter-metal dielectrics in the fabrication of integrated circuits. With the recent development of organic photonics, various polymeric materials, including homopolymers, block copolymers, polymeric hydrogels, and inorganic/

organic hybrids, have been used in optical band-gap systems. In particular, various conjugated polymers of alternating single and double bonds with delocalized π -electrons along their backbones have been synthesized to show the processing advantages of plastics and the optoelectronic properties of inorganic semiconductors or metals.^[1] Having a conjugated all-carbon structure arranged in a concentric elongated nanotube form, carbon nanotubes may be regarded as three-dimensional (3D) conjugated polymers and they also exhibit interesting electronic, photonic, magnetic, and mechanical properties attractive for optoelectronic applications.^[2,3]

In order to fabricate high-performance electronic and/or photonic devices based on conjugated polymers and carbon nanotubes, however, one often needs to align and/or pattern them in a similar fashion to silicon or metals in conventional semiconducting devices. Therefore, the surface and interface control of conjugated polymers and carbon nanotubes is a key prerequisite for many practical applications. Among the variety of techniques that are useful for surface and interface control, including photolithography,^[4,5] laser ablation,^[6] scanning probe,^[7] self-assembly,^[8] and polymeric phase separation,^[9] plasma processes have become very attractive approaches for introducing either region-specific functional surface groups (via plasma treatment) or

smooth and pinhole-free functional polymer layers (via plasma polymerization).

The plasma generation occurs when a low pressure of gaseous monomer (<10 Torr) is exposed to a radio-frequency electric field (radio-frequency band: kHz-GHz). During the glow-discharge process, excited electrons, ions, and free radicals are generated with high reactivity towards the surface, which could cause surface modification in the case of plasma treatment, and polymer deposition in the case of plasma polymerization. Although plasma polymerization normally produces cohesive, adhering, pinhole-free, and electrically insulating organic thin films with potential applications in optical wave-guides, the preparation of



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Hao Jiang is the chief scientist of Materials Sci & Tech Applications, LLC, and currently working at Air Force Research Laboratory as an on-site principal scientist. He received his BS and MS in Fiber Chemistry and Technology from China Textile University, and his Ph.D. degree in Materials Science and Engineering from the Johns Hopkins University. Before he came to the Materials and Manufacturing Directorate, AFRL, he worked in Georgia Tech as a postdoctoral fellow for two years. For 40 years, Jiang has been actively involved in the research and development of the advanced technology and processing for high performance polymer fibers and thin films. In recently 10 years, his research is focused on the fabrication of organic photonic and dielectric thin films by new techniques such as plasma enhanced chemical vapor deposition and molecular self-assembly. He is responsible for the programs associated with PECVD polymer films and coatings for optical, dielectric, and space applications at AFRL/MLPJ and AFRL/PRPE.



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semiconducting plasma-polymer films for optoelectronic devices has also been demonstrated recently. Apart from the preparation of plasma-polymer films with electronic and photonic properties, plasma-patterning techniques have also been developed.^[2] Since the plasma process involves sub-molecular species, the spatial resolution of plasma patterns are limited mainly by the structure and resolution of the physical mask used. Because of the highly cross-linked structure intrinsically associated with the plasma deposits, plasma materials/devices often show a superb environmental stability towards high temperature, intensive light, and strong electric fields.^[2] The plasma technique is a highly generic method, which ensures that the surface-engineering methodology developed in a particular case can be readily transferred to many other systems. In this feature article, we will present recent developments of the plasma processes for controlled surface engineering and device fabrication of optoelectronic polymers and carbon nanotubes by discussing several selected examples from our own work. Reference is also made to other complementary work as appropriate.

Plasma Processes for Controlled Surface Engineering and Device Fabrication of Optoelectronic Polymers

Plasma Polymerization and Patterning of Conducting Polymers

Although plasma polymerization normally produces electrically insulating organic films, it has recently been employed to produce conducting polymer films and for the micropatterning and microfabrication of electroactive polymers. Among many conducting polymers, polyaniline has attracted a great deal of attention because of its exceptional electronic and photonic properties with good environmental stability.^[2] Polyaniline can be synthesized in several different oxidation states from the fully reduced leucoemeraldine base (Figure 1a), through the half-oxidized emeraldine base (Figure 1b), to the fully oxidized pernigraniline base (Figure 1c). The emeraldine base form of polyaniline could be doped by protonic acids such as HCl (Figure 1d) to become electronically conducting.^[1,10]

We performed the plasma polymerization of aniline onto various substrates using a power input between 10 and 50 W and an excitation frequency in the range of 125–325 kHz.^[10] Unlike polyaniline films formed by electrochemical or chemical polymerization, the smooth plasma polyaniline films thus prepared are free from oxidant and solvent, and showed some improved physico-chemical characteristics (e.g., mechanical and environmental stability). Conductivity of the polyaniline plasma film can be enhanced by three orders of magnitude in a controllable fashion through HCl treatment, implying that there is considerable room for tailoring the physical

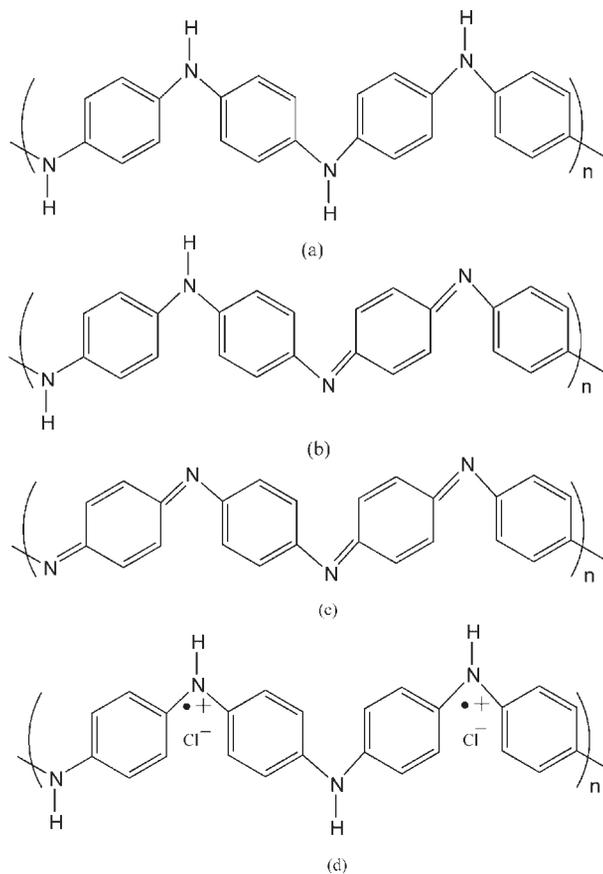


Figure 1. Repeat unit of polyaniline: (a) leucoemeraldine base, (b) emeraldine base, (c) pernigraniline, and (d) emeraldine hydrochloride doped salt.

properties of the plasma film (e.g., different conductivity values can be obtained by controlling the level of HCl treatment) for many potential applications, ranging from electromagnetic shielding to corrosion inhibition. Apart from the plasma-polymerized polyaniline, certain other conducting polymer films, such as polypyrrole^[11] and polythiophene,^[12] have also been prepared by plasma polymerization. In particular, polypyrrole thin films were produced by plasma polymerization of pyrrole/I₂ under 5 mTorr and 13.56 MHz.^[11] It was demonstrated that a ring-opening reaction mechanism dominated the discharge-driven process to form the deposited films. The resulting polypyrrole films doped with iodine have a film thickness in the range of 4.9–19.8 μm and conductivity between 10⁻⁹–10⁻³ S · cm⁻¹.

Along with the preparation of electroactive plasma-polymer films, plasma techniques have also been applied to pattern formation. In this context, we have developed surface patterns with region-specific characteristics by the plasma polymerization of appropriate monomers in a patterned fashion. Following the steps for the plasma-patterning process given in Figure 2(a), for example, we have prepared surface patterns by the patterned plasma

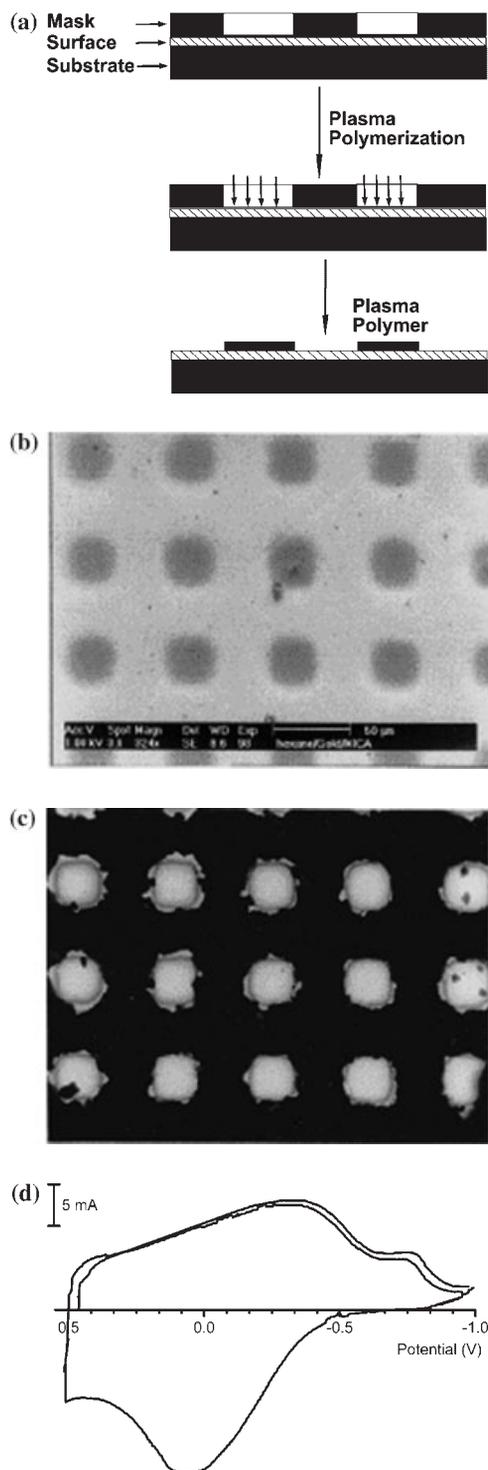


Figure 2. (a) Schematic representation of pattern formation by the radio-frequency glow-discharge plasma techniques; (b) a typical SEM micrograph of gold-coated mica sheets patterned by the hexane plasma polymer with a TEM grid consisting of square windows as the mask; (c) optical microscopy image of a polypyrrole pattern electrochemically polymerized onto a platinum-coated mica surface pre-patterned by the hexane plasma polymer; (d) typical cyclic voltammogram of the polypyrrole patterns on platinum at $100 \text{ mV} \cdot \text{s}^{-1}$ in an aqueous solution containing 0.1 M sodium perchlorate.^[13]

polymerization of hexane on a gold-coated mica surface (Figure 2b). In Figure 2b, the dark areas represent hexane plasma polymer and the bright regions are associated with the plasma-polymer-free gold surface.^[13] By extension, we developed a versatile method for obtaining patterned, conducting polymers by first depositing a thin patterned non-conducting (e.g., hexane) plasma-polymer layer onto a metal-sputtered electrode, and then performing electro-polymerization of monomers (e.g., pyrrole, aniline) within the regions not covered by the patterned plasma-polymer layer. Figure 2c represents a typical reflection light microscopic image of a polypyrrole pattern electrochemically polymerized onto platinum-coated mica sheets pre-patterned with the freshly prepared hexane plasma polymer. It shows the same features as the plasma pattern of Figure 2b, but with inverse intensities. The bright regions characteristic of the uncovered metal surface in Figure 2b become dark in Figure 2c because of the presence of a dark layer of the newly electropolymerized polypyrrole film. The bright regions in Figure 2c represent a more reflective surface associated with the hexane plasma polymer.

The cyclic voltammogram of the polypyrrole pattern shown in Figure 2c is given in Figure 2d, which shows a quasi-reversible redox process with two reduction peaks in an aqueous solution of sodium perchlorate. The first reduction peak of Figure 2d is attributable to the polarons in the electrochemically doped polypyrrole film, while the second reduction peak indicates the co-existence of a dicationic species (i.e., bipolarons).^[13] Therefore, the cyclic voltammogram measurements clearly indicate that the polypyrrole patterns thus prepared are electrochemically active.

More recently, we have also produced conducting polymer microcontainers in a patterned fashion by pre-patterning the working electrode surface with non-conducting polymers through plasma patterning.^[14] Figure 3a schematically shows the steps for the patterning process by the plasma method. Prior to the patterning, the stainless-steel electrode was cleaned by an aqueous solution of HNO_3 (15.8 M after being diluted to $1:1 \text{ v/v}$, $\text{H}_2\text{O}/\text{HNO}_3$) under ultrasonication for 30 min, followed by thoroughly washing with distilled water and acetone. For the plasma patterning, non-conducting plasma-polymer patterns were produced on the stainless-steel electrode surface by plasma polymerization of an appropriate monomer (e.g., hexane at 150 kHz and 0.3 Torr for 2 min) through a mask (Figure 3a). The electrode with the pre-patterned non-conducting plasma-polymer film was then used for region-specific electrodeposition of polypyrrole microcontainers by the so-called “soap bubble” template. This involved the electrochemical polymerization of pyrrole around the wall of the gas bubbles generated within the plasma-polymer-free regions on the working electrode by the electrolysis of H_2O in the presence of surfactant (i.e., β -naphthalenesulfonic

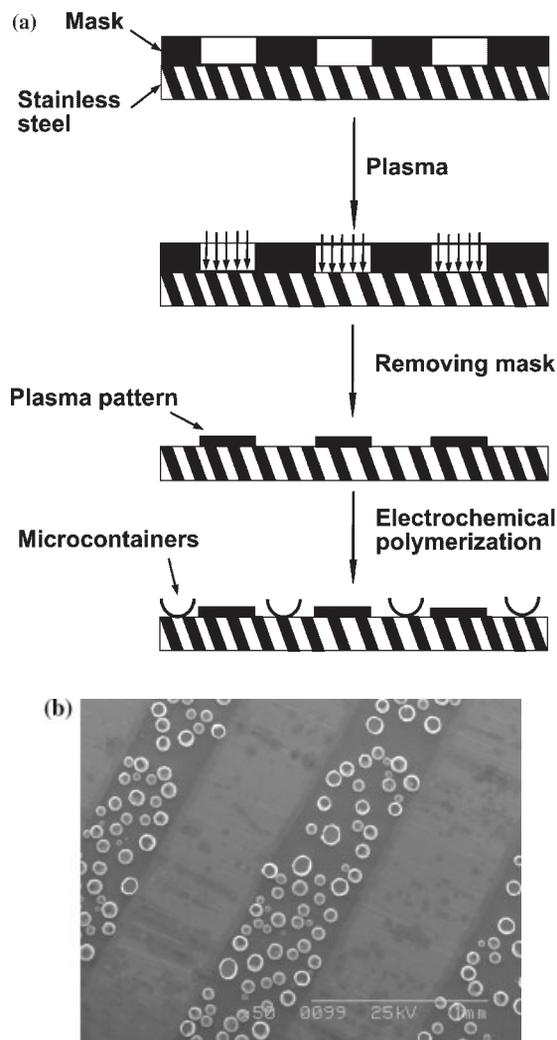


Figure 3. (a) Schematic illustration of the procedure for fabricating patterns of polypyrrole microcontainers by plasma patterning. (b) SEM image of polypyrrole microcontainer pattern obtained by plasma patterning. The parameters for preparing polypyrrole microcontainers are as following. Voltammetric scanning from -1.0 to -1.65 V, scanning rate of $20 \text{ mV} \cdot \text{s}^{-1}$, 1 cycle to generate the soap-bubble template; voltammetric scanning from 0.5 to 1.1 V, scanning rate of $50 \text{ mV} \cdot \text{s}^{-1}$, 3 cycles to perform electropolymerization. The electrolyte aqueous solution is 0.25 M pyrrole with 0.4 M β -naphthalene sulfonic acid sodium salt.^[14]

acid, β -NSA).^[14] Figure 3b shows a typical scanning electron microscopy (SEM) image of the microcontainer patterns generated on a stainless-steel electrode by the plasma-patterning method. As can be seen in Figure 3b, polypyrrole microcontainers can be region-specifically electrodeposited onto the electrode pre-patterned with non-conducting plasma-polymer film. The patterned conducting polymer microcontainers thus prepared may find applications in certain sensing chips and optoelectronic devices.

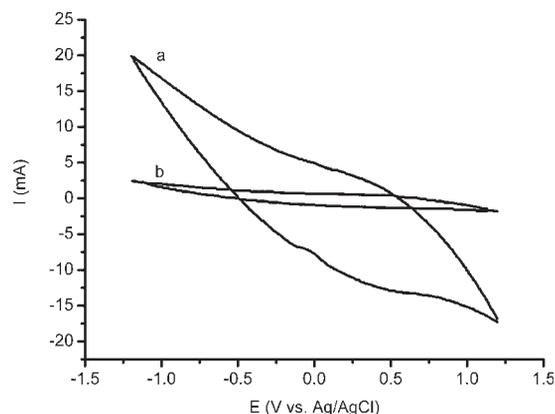


Figure 4. Cyclic voltammograms of a polypyrrole film with (a) microcontainers and (b) a flat polypyrrole film in an aqueous solution of NaClO_4 (0.1 M) at a scanning rate of $100 \text{ mV} \cdot \text{s}^{-1}$.^[14]

To demonstrate the potential applications of the polypyrrole microcontainers, the cyclic voltammetric response of a polypyrrole microcontainer electrode was measured. As shown in Figure 4, the electrode deposited with the polypyrrole microcontainers showed a stronger redox response than that without because of the large surface areas associated with the microcontainers, which is advantageous for their use for sensing applications.^[14]

Furthermore, some conjugated polymers have also been directly deposited onto plasma-patterned surfaces by self-assembly. For example, we have prepared light-emitting polymer patterns by first depositing hydrophilic (i.e., acetic acid) plasma patterns onto hydrophobic substrates (e.g., perfluorinated ethylene-propylene copolymer films), and then performed a selective adsorption from a solution of a 2,5-substituted poly(*p*-phenylene vinylene) derivative with methoxy-terminated oligo(ethylene oxide) side chains (i.e., EO_3 -PPV, $\text{EO}_3 = \text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$, Figure 5).^[1,15] The driving force for the pattern formation, in this particular case, was the polar-polar interaction between the EO_3

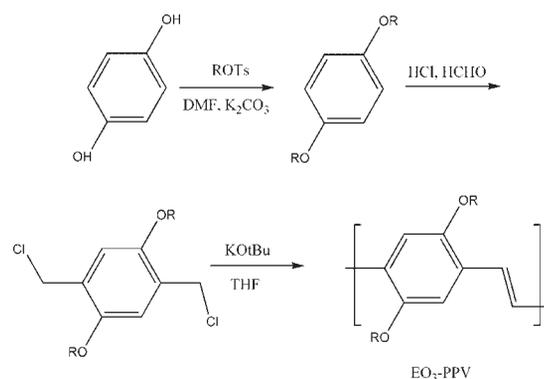


Figure 5. Synthesis of EO_3 -PPV via a modified Gilch route [$\text{R} = (\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$].

side chains and the micropatterned hydrophilic plasma polymer. Under the fluorescence microscope, the EO₃-PPV-patterned regions gave fluorescence emissions characteristic of the conjugated structure.^[15]

Plasma Process for the Fabrication of Polymer Photonic Devices

Vapor-deposition techniques, including plasma polymerization and chemical-vapor deposition, are solvent-free, low-temperature, thin film-forming processes with a clean working environment. They can be used to circumvent problems possibly associated with various solution-processing methods (e.g., the deterioration of the mechanical properties of solution-cast polymer films by trapped solvent, and difficulty in choosing suitable solvent(s) for preparing pinhole-free single layer or multilayer polymer thin films). In fact, plasma-enhanced chemical-vapor deposition (PECVD) has been used to produce highly crosslinked films with continuously varying refractive indices for photonic devices. Moreover, PECVD has also been demonstrated to be useful for co-depositing two precursors simultaneously to create an average refractive index somewhere between the starting materials, which could potentially lead to a continuous change in the refractive index profile for an organic film. In addition, PECVD is amenable to deposition on substrates with complicated geometries. Therefore, PECVD has many potential advantages for making various single-layer and multilayer optical thin films with different refractive index profiles for a wide range of applications, including optical filters, antireflective coatings, and optical waveguides.^[16,17]

Indeed, PECVD has been widely used for preparing thin non-active barrier layers between photonic films in photonic devices. In this context, Bunning and co-workers^[18] have used a fully cured, dye-free siloxane layer as a substrate for the plasma deposition of a barrier layer between different stacks. The plasma-polymerization process was carried out by discharging an argon flow at a rate of 100–200 cc · min⁻¹ under 1 Torr vacuum, 13.56 MHz, and 10 W power, followed by introducing a calibrated flow of hexamethyldisiloxane 20 cm downstream from the plasma afterglow region. Depending on the polymerization time, the plasma-polymerization process produced 60–240 nm thick films. The plasma-polymerized hexamethyldisiloxane film at the interface of two polymer layers doped with and without dye molecules (i.e., zinc octabromylporphyrin) was found to be an effective barrier to diffusion of the dye molecules because of the high degree of crosslinking. As shown in Figure 6a, the polarizing optical microscope image of the crosslinked polysiloxane bilayer without interface treatment shows that the dye molecules diffused into the initially non-doped layer through the interface. With a plasma-deposited hexamethyldisiloxane film as a barrier layer at the interface, however, the diffusion of dye

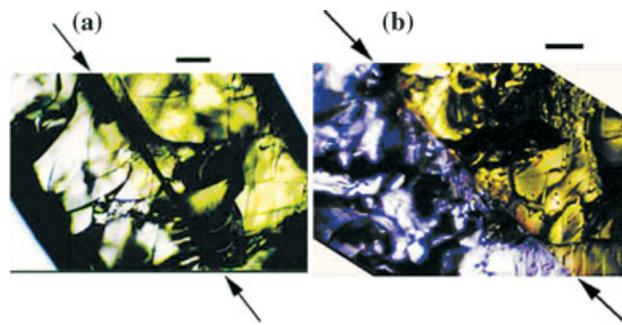


Figure 6. Polarizing optical microscopy of two crosslinked polysiloxane layer, one containing chromophore (top right) and one initially containing no chromophore (bottom left) (a) without and (b) with a 180 nm plasma-polymerized hexamethyldisiloxane film deposited at the interface. The arrows mark the interface between the two polysiloxane layers. Both of the samples were photographed 48 h after processing. The scale bar corresponds to 250 μm .^[18]

molecules is dramatically inhibited, as indicated by the absence of green color in the undoped layer (Figure 6b).^[18]

Apart from the deposition of non-active barrier layers at interfaces in photonic devices, PECVD has also been used to produce single-layer optical polymers, such as fluorocarbon plasma polymers^[19,20] and amorphous carbonaceous (a-C:H) films.^[21,22] For instance, Labelle and Gleason^[19] have deposited fluorocarbon films by pulsed PECVD using CH₂F₂, C₂H₂F₄, and CHClF₂ as plasma monomers. It was found that the pulsed plasma of all the three monomers gave plasma films with dielectric constants of 2.4 and loss tangents in the order of 10⁻². In order to form a-C:H plasma films, a dual-mode (surface wave-coupled microwave and capacitively coupled radio frequency) PECVD was used to combine the high density of excited species in the post-discharge of a microwave plasma with the ion bombardment provided by the radio frequency plasma.^[23] The extinction coefficient at 3.5 eV of the a-C:H films fabricated by the dual-mode PECVD method increases with the radio frequency power, as indicated by kinetic ellipsometry measurements, presumably because of the increase of clustering of the trigonal sp² bonding configurations.

Monomers with a wide variety of chemistries are amenable to plasma polymerization using the PECVD process. This allows for a wide range of optical properties to be obtained. Shown in Figure 7 are the dispersion curves for the real and imaginary parts of the refractive index (RI) for a variety of monomers recently polymerized. Absorption coefficients that span three orders of magnitude and RIs that span >0.3 can be obtained. Moreover, films with widely varying chemical and surface properties but with similar optical properties can be formed. Combinations of the properties can also be obtained either through a serial, step homopolymerization process or through simultaneous copolymerization of multiple monomers.

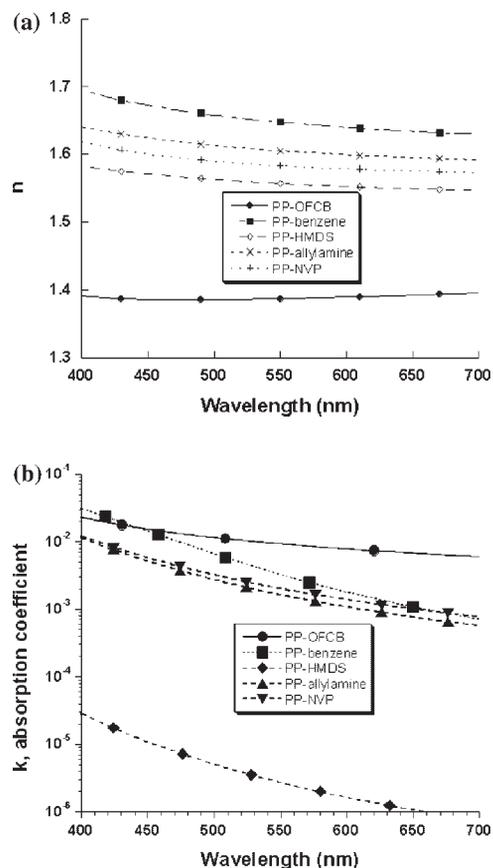


Figure 7. The dispersion curves for the (a) real and (b) imaginary parts of the refractive index for a variety of plasma polymers from various monomers.

Since single layer optical films seldom meet the critical requirements for controlling the polarization, wavelength, amplitude, and direction of the light sources, the formation of multilayer optical films is often necessary in many photonic devices. Using PECVD with different organic precursor materials, Bunning et al.^[24] have also prepared a multilayer optical interference film. In a typical experiment, these authors excited gas-phase molecules of octafluorocyclobutane (OFCB) and benzene with an argon plasma in a flowing afterglow reaction chamber to form dense, pinhole-free, crosslinked polymer films on a variety of substrates. The plasma OFCB polymer film yields a refractive index of 1.40, whereas plasma benzene polymer exhibits a refractive index of 1.61 at 500 nm. A ten-bilayer stack of alternating high and low refractive index was fabricated by sequential deposition of high and low refractive index layers at approximately $\frac{1}{4}$ wavelength optical thickness. Figure 8 gives SEM micrographs of the cross-section of the 10-bilayer stack (fractured in liquid nitrogen), which clearly shows cohesive and densely packed individual layers. It has been demonstrated that the wavelength of extinction for this multiplayer optical interference film matches the design wavelength, indicating a good control of the optical thickness, as shown in Figure 9. The ellipso-

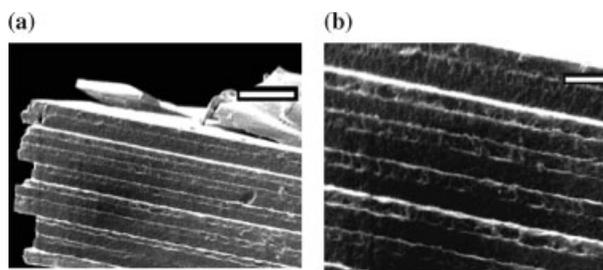


Figure 8. Scanning electron micrographs of the fractured cross-section of the multilayer stack consisting of alternating high and low refractive index films. Scale bars correspond to 1.5 μm and 600 nm for (a) and (b), respectively.^[24]

metry results of the individual components indicate that a small finite absorption is present and thus harmonics were observed, which also indicated a good agreement with the overall QW (quantum well) stack design. Also observed are the ripples characteristic of interference events with the substrate. The depth of the notch for this number of layers and refractive index contrast is low because of the finite values of absorption present in each material. The positions of the peaks and the magnitude of the notch are close, which is remarkable given the serial nature of the deposition process. This indicates that the PECVD technique can be used to deposit organic optical films with good thickness control.^[24]

More recently, Bunning and co-workers^[25] have successfully applied the PECVD technique to the copolymerization of two monomers (e.g., benzene and OFCB) to fabricate photonic copolymer films with a gradient index. In this case, the composition of these plasma copolymer films could be controlled by changing the feeding rates of the monomers, leading to a linear dependence of the refractive index on the film composition characterized by the fluorine/carbon ratio (Figure 10). Hence, the plasma-copolymerization process is promising to prepare

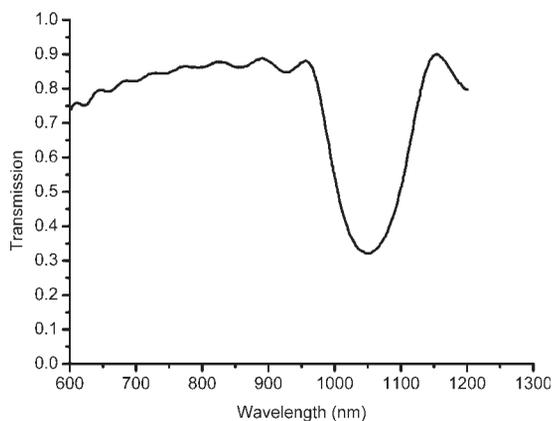


Figure 9. Transmission spectra of a 10 bilayer stack of plasma-polymerized benzene and OFCB sequentially deposited. The dip in the transmission is caused by an optical band-gap attributable to multilayer interference.

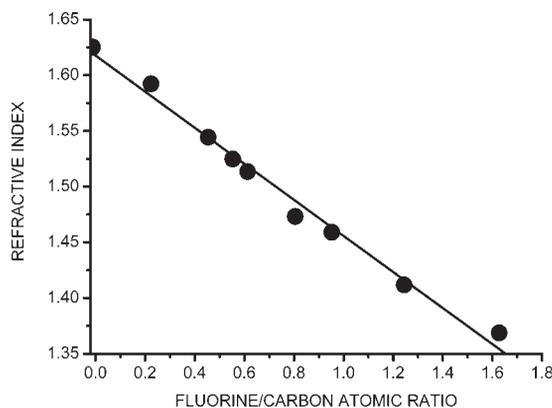


Figure 10. Linear dependence of the refractive index (at 632.8 nm) on the composition ratio of each film. The F/C atomic ratio in the resultant films was determined by XPS.^[25]

gradient-index films of well-controlled properties in the nanometer range with a Δn greater than 0.3.

Access to any refractive index between the extremes, enabled by plasma copolymerization, allows for complicated optical designs such as multilayer anti-reflection (AR) coatings to be formed as shown in Figure 11.^[25] In these cases, the optical thickness (RI times the physical thickness) is controlled to the nanometer length scale.

As can be seen from the above discussion, the PECVD process can be viewed as a promising approach for the fabrication of single-layer, multilayer, and gradient refractive index films from organic monomers for various photonic applications. Here, the layered structures and their interfaces play important roles in regulating the performance of the photonic devices. X-ray reflectivity and neutron reflectivity studies on some optical multilayers made by the PECVD approach indicate that their interfaces are extremely sharp; even sharper than that which is often achievable with the self-assembly of block copolymers or deposition techniques in which the polymer layer contacts

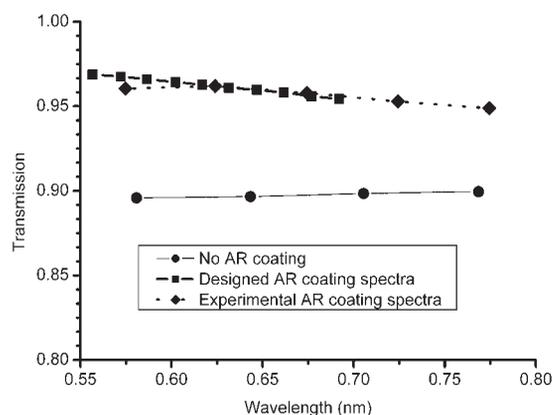


Figure 11. Optical transmission spectra of F2 glass before and after deposition of a plasma-polymerized multilayer (6) anti-reflection coating. A substantial increase in transmission is observed and the fit to the designed spectra is very good.

with a fluid state. Typically, the average-interface width between layers made from different precursors (benzene, deuterated benzene, and octafluorocyclobutane) was found to be about 4.0 nm, while the layer/layer interfaces are generally 2–3 times broader than the layer/air interface. Polymeric fluorocarbon films deposited on an Si substrate from an octafluorocyclobutane monomer even show uniform scattering length density with depth except for a region of molecular thickness adjacent to the substrate, whereas the plasma-deuterated benzene films show uniform density throughout the film thickness.^[26] Therefore, there is no doubt that the plasma technique will have potential implications for making high-quality organic optical films for fascinating photonic applications. The ease with which micropatterning of organic materials can be achieved by the plasma technique could impart additional benefits to this approach.

Plasma Processes for Controlled Surface Engineering and Device Fabrication of Carbon Nanotubes

Plasma-Enhanced Chemical-Vapor Deposition (PECVD) and Patterning of Carbon Nanotubes

PECVD for the Synthesis of Non-Aligned and Aligned Carbon Nanotubes

In addition to the above-mentioned preparation of organic thin films for electronic and photonic applications, the PECVD technique has also been widely used for the synthesis of non-aligned and aligned carbon nanotubes in a patterned and non-patterned fashion. For instance, non-aligned carbon nanotubes have been synthesized by microwave PECVD of a mixture gas containing benzene, hydrogen, and argon at a relative low temperature ($<520^\circ\text{C}$) using Fe (or Co, Ni)/ $\gamma\text{-Al}_2\text{O}_3$ as catalysts. By regulating the type of catalyst, the microwave incident power, the ratio and flux of the precursors, helical or planar spiral carbon nanotubes can be produced by the PECVD technique.^[27] Non-aligned carbon nanotubes have also been prepared on silicon substrates using an iron catalyst by a low radio frequency PECVD technique.^[28]

Apart from the production of non-aligned carbon nanotubes, the PECVD technique has also been used to grow aligned carbon nanotubes effectively because of the dc electric field applied to the growth surface.^[29–33] In this regard, Huang et al.^[34] have deposited highly oriented multiwalled carbon nanotubes on polished polycrystalline and single-crystal nickel substrates by plasma-enhanced hot-filament chemical-vapor deposition of acetylene at temperatures below 666°C in the presence of ammonia gas. Depending on the growth conditions, the aligned carbon nanotubes thus prepared can have a diameter in the range of 10 to 500 nm and length from 0.1 to 50 μm . The plasma intensity was found to be critical in determining the

nanotube aspect ratio (length to diameter) and the height distributions within a given nanotube film.^[34] PECVD technique has also been used for preparing patterned multiwalled carbon nanotubes on pre-patterned Ni catalysts generated by shadow masking or e-beam lithography.^[35]

Plasma-Induced Patterning of Non-Aligned and Aligned Carbon Nanotubes

In our investigation on the microfabrication of carbon nanotubes, we have not only used certain plasma-polymerized polymer patterns for region-specific growth of the aligned carbon nanotubes, but have also developed a versatile method for making patterns of non-aligned carbon nanotubes.^[36,37] In order to pattern non-aligned carbon nanotubes, the FePc-generated carbon nanotubes were treated by HNO_3 to introduce $-\text{COOH}$ groups.^[36] Plasma-induced surface patterns of $-\text{NH}_2$ groups either by non-depositing plasma treatment or by plasma polymerization were generated on a substrate (e.g., quartz glass plate, mica

sheet, polymer film), and then followed by region-specific adsorption of the COOH -containing carbon nanotubes from an aqueous dispersion onto the plasma-induced $-\text{NH}_2$ surface, presumably because of the polar-polar interaction between the plasma-patterned $-\text{NH}_2$ and the $-\text{COOH}$ groups (Figure 12A(a)).

Figure 12B(a) reproduces an SEM image of the COOH -containing carbon nanotubes region-specifically adsorbed (ca. $2.5 \text{ mg} \cdot (10 \text{ mL H}_2\text{O})^{-1}$) onto a mica sheet pre-patterned with the heptylamine-plasma polymer (200 kHz, 10 W, and a monomer pressure of 0.13 Torr for 30 s). The adsorbed carbon nanotubes are clearly evident upon inspection of the plasma-patterned areas of Figure 12B(a) under a higher magnification (inset of Figure 12B(a)). The corresponding high-magnification SEM image for the plasma-polymer-free areas reveals an almost featureless smooth surface characteristic of a mica sheet. No adsorption of the carbon nanotubes was observed in a control experiment when a pure mica sheet was used as the substrate.

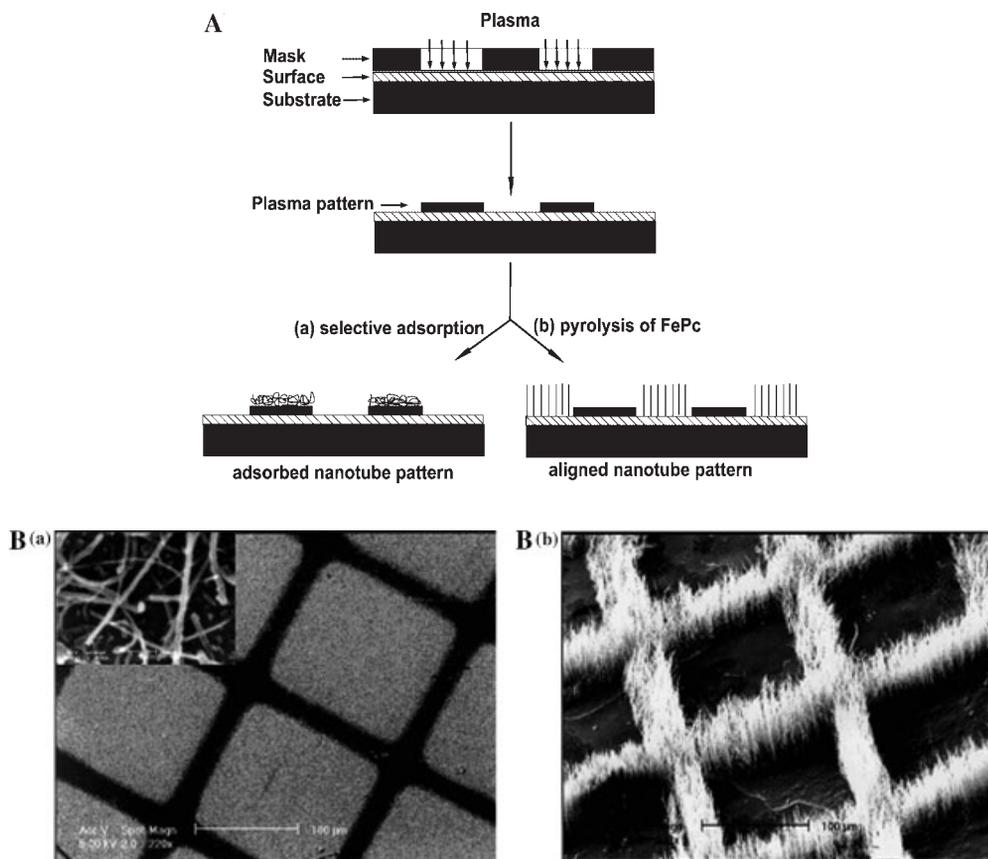


Figure 12. (A) Schematic illustration of the procedure for fabricating patterns of carbon nanotubes by (a) plasma activation followed by region-specific adsorption; (b) plasma polymerization followed by nanotube growth. (B) SEM images of (a) adsorbed COOH -containing carbon nanotubes (within the squared areas) on a heptylamine-plasma patterned mica sheet (inset gives a higher magnification image of the plasma covered areas, showing the individual adsorbed carbon nanotubes),^[36] and (b) aligned nanotube arrays growing out from the plasma-polymer-free regions on a hexane-plasma-polymer-patterned quartz plate.^[37]

Figure 12A(b) shows the steps for fabricating patterns of carbon nanotubes by plasma polymerization followed by nanotube growth. Figure 12B(b) shows an SEM image of the aligned nanotube micropatterns prepared on an hexane plasma-polymer pre-patterned quartz plate. The highly crosslinked structure of plasma-polymer films^[38,39] could ensure the integrity of the plasma-polymer layer to be maintained, even without carbonization, at high temperatures necessary for the nanotube growth from FePc.^[37] Therefore, the carbonization process involved in our work on photolithographic^[40] and soft-lithographic^[41] patterning of the aligned carbon nanotubes can be completely eliminated in the plasma-patterning process. Owing to the generic nature characteristic of the plasma polymerization, many other organic vapors could also be used equally well to generate plasma-polymer patterns for the patterned growth of the aligned carbon nanotubes.

More recently, we have found that micropatterns of the perpendicularly-aligned carbon nanotubes can be prepared by simply pressing a Scotch tape pre-patterned with a non-adhesive layer onto the FePc-generated carbon nanotube film, followed by peeling off the nanotubes together with the Scotch tape from the quartz substrate in a dry state (designated as a “dry contact transfer”).^[42] The dry contact transfer could not only maximize the retention of the structural integrity of the perpendicularly aligned carbon nanotubes after the contact transfer but also allow the region-specific interposition of other component(s) into the discrete areas interdispersed in the patterned nanotube structure.

In particular, we have prepared multicomponent, interposed, carbon-nanotube micropatterns by the dry contact transfer of the FePc-generated, perpendicularly aligned carbon nanotubes onto a Scotch tape pre-patterned with a thin layer of heptylamine-plasma-treated silver, followed by region-specific adsorption of acid-oxidized carbon nanotubes onto the plasma-treated areas interdispersed in the patterned nanotube structure (Figure 13a).

As shown in Figure 13b, both the contact, transferred, aligned carbon nanotubes and the adsorbed, non-aligned carbon nanotubes are well registered in their respective areas.

Plasma Process for the Fabrication of Carbon Nanotube Sensors

Plasma Activation of Carbon Nanotubes for Chemical Modification and for DNA Sensing

The use of carbon nanotubes, either in aligned or non-aligned form, for many applications, including as the reinforcement material for making advanced polymer composites and as biosensors in biomedical devices, inevitably requires the modification of their surface characteristics to meet the specific requirements for particular applications. Given that the alignment is an additional advantage for the use of carbon nanotubes in many devices, a particularly attractive option is the surface modification of the carbon nanotubes while largely retaining their structural integrity.

In this context, we have developed a plasma approach for the chemical modification of carbon nanotubes by activating them with an acetaldehyde plasma followed by chemical reactions characteristic of the plasma-generated functional groups.^[43] For instance, aminodextran chains have been successfully immobilized onto acetaldehyde-plasma-treated, aligned carbon nanotubes through the formation of a Schiff-base linkage, which was further stabilized by reduction with sodium cyanoborohydride (Figure 14).^[43–45] The polysaccharide-grafted nanotubes are very hydrophilic, and potentially useful for many biological applications.

To demonstrate the potential use of the plasma-modified, aligned carbon nanotubes for biosensing applications, we have also carried out acetic acid-plasma treatment on gold-supported, aligned carbon nanotubes generated from the pyrolysis of iron(II) phthalocyanine,^[40] followed by

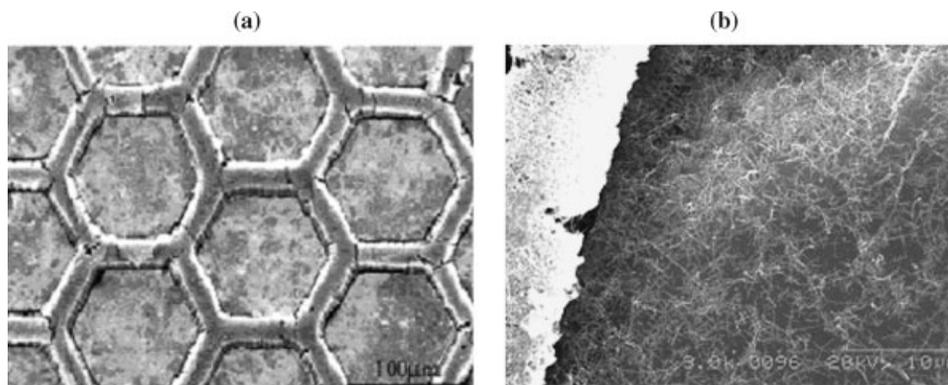


Figure 13. SEM micrographs of the multicomponent interposed carbon nanotube micropatterns with non-aligned carbon nanotubes region-specifically adsorbed between aligned carbon nanotube patterns. (a) A low magnification image and (b) a high magnification image, showing individual adsorbed carbon nanotubes within the hexagonal regions of Figure 13(a).^[42]

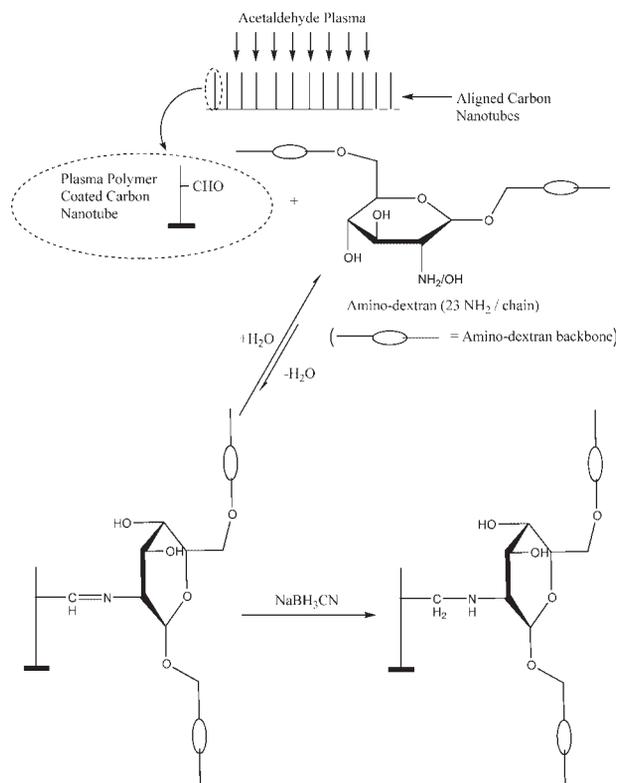


Figure 14. Reaction scheme for the covalent immobilization of aminodextran chains onto acetaldehyde-plasma activated carbon nanotubes. For reasons of clarity, only one of the many plasma-induced aldehyde surface groups is shown for an individual nanotube.^[43]

grafting single-strand DNA (ssDNA) chains with an amino group at the 5'-phosphate end (i.e., [AmC6] TTGACAC-CAGACCACTGGT-3', **I**) onto the plasma-induced -COOH group by amide formation in the presence of EDC [1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride] coupling reagent. Complementary DNA (cDNA) chains pre-labeled with ferrocenecarboxaldehyde, FCA (designated as: [FCA-C6] ACCAGTTGGTCTGG-TGTCAA-3', **II**) were then used for hybridizing with the surface-immobilized oligonucleotides to form double strand DNA (dsDNA) helices on the aligned carbon nanotube electrodes, as shown in Figure 15.^[46]

The performance of the aligned carbon nanotube-DNA sensors for sequence-specific DNA diagnoses was demonstrated in Figure 16. The strong oxidation peak seen at 0.29 V in curve (a) of Figure 16 is attributable to ferrocene and indicates the occurrence of hybridization of FCA-labeled cDNA (**II**) chains with the nanotube-supported ssDNA (**I**) chains, leading to a long-range electron transfer from the FCA probe to the nanotube electrode through the DNA duplex. In contrast, the addition of FCA-labeled, non-complementary DNA chains (i.e., [FCA-C6]CTCCAG-GAGTCGTCGCCACC-3', **III**) under the same conditions did not show any redox response of FCA (curve (b) of Figure 16). Subsequent addition of target DNA chains (i.e., 5'-GAGGTCCCTCAGCAGCGGTGGACCAGTTGGTCT-GGTCAA-3', **IV**) into the above solution, however, led to a strong redox response from the FCA-labeled DNA (**III**) chains (curve (c) of Figure 16) because the target DNA

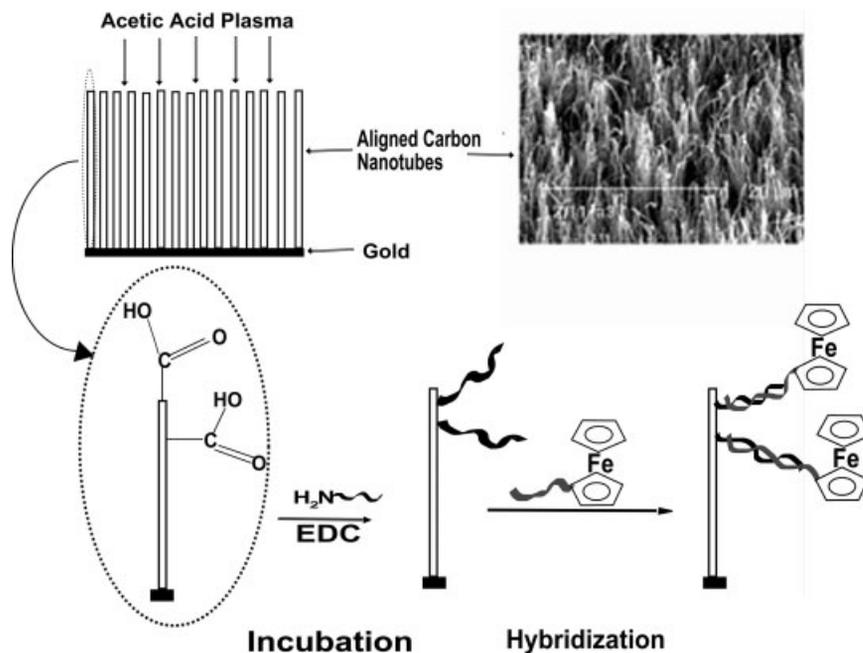


Figure 15. A schematic illustration of the aligned nanotube-DNA electrochemical sensor. The upper right SEM image shows the aligned carbon nanotubes after having been transferred onto a gold foil. For reasons of clarity, only one of the many carboxyl groups is shown at the nanotube tip and wall, respectively.^[46]

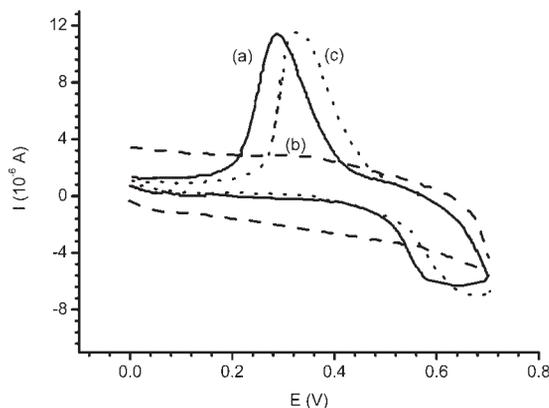


Figure 16. Cyclic voltammograms of the ssDNA (I)-immobilized aligned carbon nanotube electrode after hybridization with FCA-labeled complementary DNA (II) chains (a), in the presence of FCA-labeled noncomplementary DNA (III) chains (b), and after hybridization with target DNA (IV) chains in the presence of the FCA-labeled non-complementary DNA (III) chains (c). All the cyclic voltammograms were recorded in 0.1 M H_2SO_4 solution with a scan rate of $0.1 \text{ V} \cdot \text{s}^{-1}$. The concentration of the FCA-labeled DNA probes is $0.05 \text{ mg} \cdot \text{mL}^{-1}$.^[46]

(IV) contains complementary sequences for both DNA (I) and DNA (III) chains. These results clearly indicated that the plasma-modified, ssDNA-attached, aligned carbon nanotubes are of practical applications as highly sensitive DNA sensors because of the large surface area associated with the nanotube structure.

Plasma Etching for the Controlled Opening of Aligned Carbon Nanotubes for Flow Control and Sensing

We have previously reported that H_2O plasma can be used to effectively etch many substrates including even mica sheets.^[47] Recently, we found that the H_2O -plasma-etching technique can also be used to selectively open the top end-caps of the aligned carbon nanotubes without any observable structural change of the sidewalls under appropriate plasma conditions.^[48] Figure 17a shows a typical closed structure of the aligned carbon nanotubes with encapsulated Fe rods at their tips. In contrast, Figure 17b clearly shows the removal of the top end-caps from the aligned nanotubes by the H_2O plasma etching.

In an independent but somewhat related study, Hinds et al.^[49] have also used the H_2O -plasma-etching technique for etching an aligned carbon nanotube/polystyrene nanocomposite film. In this study, the H_2O plasma etching was performed for 7 min at a power of 200 watts under 0.6 Torr while maintaining a substrate temperature of 25 to 32 °C. It was found that the plasma oxidation process etched polystyrene faster than multiwalled carbon nanotubes; thus, the carbon nanotube tips were 10–50 nm above the polymer surface. The resulting membrane with the opened aligned carbon nanotubes was then demonstrated to allow the transport of $\text{Ru}(\text{NH}_3)_6^{3+}$ ions in aqueous solution at a flux of

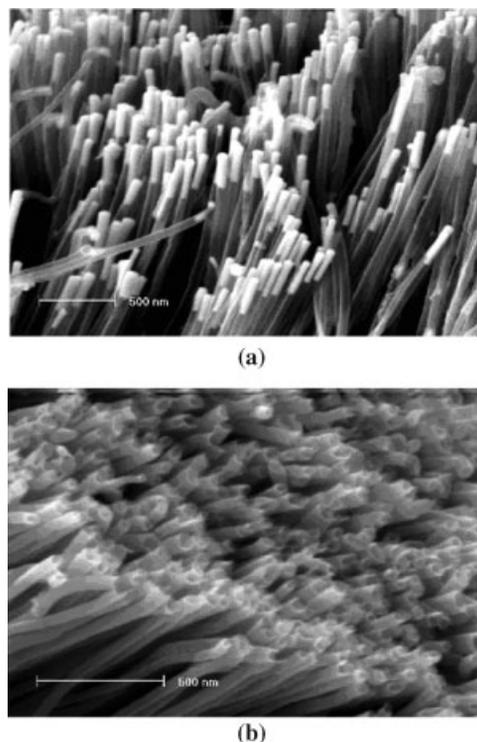


Figure 17. SEM images of an aligned carbon nanotube film before and after the H_2O -plasma etching (a) aligned nanotubes capped by Fe nanorods before plasma treatment. (b) After the H_2O plasma etching for 80 min at 250 kHz, 30 W, and 0.62 Torr.^[48]

$0.07 \mu\text{mol} \cdot \text{cm}^{-2} \cdot \text{h}^{-1}$ with a diffusion coefficient of $2.2 (\pm 0.9) \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$. In contrast, a control sample without H_2O plasma treatment didn't show ionic transport for $\text{Ru}(\text{NH}_3)_6^{3+}$ ions. Further functionalization of the open tips of the carbon nanotubes with COOH end groups and/or their derivatives could form the basis for gatekeeper-controlled chemical separations or an ion-channel mimetic sensor.

On the other hand, opened carbon nanotubes with their inner surface grafted by polymer brushes could also act as both sensor and valve for flow control since the grafted polymer chains can expand in response to a shear flow,^[50] leading to a decrease in the cross-sectional area for keeping the flux constant even when the flow rate is changed (Figure 18). Given that various stimuli-responsive (e.g., electroactive, thermal responsive) polymers are readily available, the plasma activation followed by further chemical modification approach can be viewed as potentially promising for the use of polymer-carbon nanotube

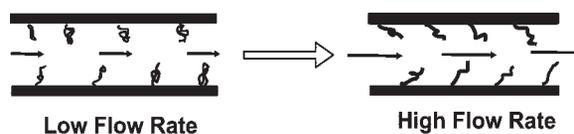


Figure 18. Schematic illustration of the polymer-grafted carbon nanotube as a sensor and valve for flow control.

composites in future electronic and fluidic devices with nanoscale features.

Conclusion

Conjugated polymers and carbon nanotubes show interesting optoelectronic properties that make them attractive for a wide range of potential applications in electronic and photonic devices. In order to fabricate useful devices, however, these materials often need to be aligned and/or micropatterned in the same way as for silicon or metals in conventional semiconducting devices. With the advances in the plasma technique, plasma processes have become very promising approaches for controlled surface/interface engineering and for fabricating future electronic and photonic devices. We have briefly summarized various plasma approaches for the microfabrication of optoelectronic polymers and carbon nanotubes useful for electronic and photonic device applications. Even this brief and somewhat incomplete survey has clearly indicated the usefulness of plasma processes for producing novel materials with controllable optoelectronic properties and region-specific characteristics with desirable features attractive for electronic and photonic device applications.

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