Multiscale Carbon Structures Fabricated by Direct Micropatterning of Electrospun Mats of SU-8 Photoresist Nanofibers

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A novel method for the direct fabrication of arrays of micropatterned polymeric and carbon nanofiber structures on any substrate is developed. First SU-8, an epoxy-based negative photoresist, is electrospun under optimized conditions to produce a layer of polymeric nanofibers. Next, this nanofibrous mat is micropatterned using photolithography, and finally, pyrolysis produces ordered arrays of microdomains containing carbon nanofibers. The nanotextured surfaces of carbon nanofibers are shown to be very hydrophobic (water contact angle ~130°). Micropatterning thus generates a substantial wettability contrast of nanofiber domains with intervening micropatches of very hydrophilic carbon (~20°) or silicon substrates.

Introduction

Carbon nanofibers have excellent mechanical and electronic properties. They are chemically inert and have a high surface area; these are properties that can be exploited in applications ranging from filters and catalysts to sensors, batteries, and fuel cells. Carbon nanofibers may also be activated and functionalized to tailor their properties to a more specific use. Because carbon nanotubes have lost some of their original luster because of expense and difficulties in exploiting them for anything other than stronger composites, carbon nanofibers are attracting increased scientific and technological attention as a perhaps less expensive and more facile way to exploit carbon properties on the nanolevel.[1−6]

The electrospinning process is a simple, versatile, and widely used method of producing nanofibers.[1−4,7−9] Among the precursors used in the synthesis of carbon nanofibers by electrospinning,[1−6] polyacrylonite (PAN)/N,N-dimethylformamide (DMF) solution is the most commonly employed. Carbon nanofibers with diameters in the range of 80−750 nm are typically obtained from this solution by electrospinning.[2,3] However, we have fabricated carbon nanofibers by electrospinning SU-8 (an epoxy-based negative photoresist) as the polymer precursor and subsequent pyrolysis of that precursor. Moreover, we show that the electrospun material retains its photoresist properties and that it can be directly patterned in a wide variety of patterns by lithography before pyrolysis. The pyrolysis of patternable organic precursors or carbon-MEMS has drawn a considerable amount of attention in the past decade;[10−14] in particular, the suitability of the resulting glassy-carbon-like material for electrochemical applications has made C-MEMS a productive research area. The pyrolysis of SU-8 nanofibers to produce carbon nanofibers will enhance the C-MEMS toolbox considerably and allow for the facile integration of high-surface-area fibers with other SU-8-derived carbon structures. This not only will allow for the making of interesting photopatternable carbon composites but also will enable the fabrication of multiscale hierarchal assemblies such as fractal-like electrodes where a high external surface area is coupled with a minimized internal resistance, which is a feature of great utility, in batteries and fuel cells.[14] The biocompatibility of SU-8-derived carbon[15] provides further motivation for the development of multiscale hierarchal scaffolds for tissue engineering and in vivo biosensors.

Patterning films of nanofiber precursor material by standard photolithographic techniques is bound to open up other applications in microelectronics, photonics, and biotechnology. There are a few studies[16−23] on patterning polymeric fibers into arrays, but

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the preparation of complex and well-defined fibrous architectures (e.g., an array of fibrous cantilevers, an array of treelike structures (fractals) made up of fibers, arrays of fibrous filters, etc.) remains a challenge. Recently, multistep microcontact printing and etching techniques have been used to pattern electrospun fibers.[24] Here, we present a very simple, generic, versatile, and direct technique to produce a wide variety of patterned polymeric and carbon fibers over large areas. We first optimized the SU-8 electrospinning parameters in order to produce a nonwoven fabric of long, continuous SU-8 nanofibers. These nonwoven fabrics were then patterned using standard photolithography to create an array of simple fiber structures such as squares and rectangles. These architectures were then pyrolyzed at 900 °C in an inert atmosphere to yield well-defined patterns of high-surface-area carbon fiber microstructures. On the basis of their high surface area and glassy-carbon-like electrochemical behavior,[10,12] these simple arrays of patterned carbon nanofibers may also be useful as electrodes for microbatteries, fuel cells, biosensors, and supercapacitors. We have also tested the wetting characteristics of the obtained fabric patterns and found that surface texture alone can dramatically modulate the wettability of the SU-8-derived carbon surface from mildly hydrophilic to nearly superhydrophobic. The possibility for easy modulation of the wetting properties of the same SU-8-derived carbon, from nanofibrous to a smooth film, makes these patterns attractive for numerous applications such as cell scaffolds, microfluidics, and biosensors.[25,26]

Experimental Section

Preparation of SU-8 Nanofibers. In the electrospinning process, a high voltage (typically 5−30 kV) is used to create an electrically charged jet of a polymer solution, which solidifies to leave a polymer fiber. The first electrode is placed in the spinning solution some distance from the second electrode (target or collector) of opposite polarity to establish the electric field. The electric field is applied to the end of a capillary tube (nozzle) that contains the polymer fluid held by its surface tension. A so-called Taylor cone forms on the nozzle because of the competing forces of the electric field and the surface tension of the solution. For liquids with a finite conductivity and without polymer solutes, charged droplets are expelled from the tip of the Taylor cone and are delivered to the collector. If the liquid consists of a polymer dissolved in the solution and the concentration of the polymer is high enough to cause molecular-chain-entanglement-induced elasticity, then a fiber rather than a droplet is drawn from the tip of the Taylor cone. In the air gap between the nozzle and the collector, the polymer solution jet undergoes a whipping process wherein the solvent evaporates, leaving behind a charged polymer fiber that randomly lies on the grounded collector. In our case, the polymer was collected on a silicon wafer attached to a grounded copper screen. An epoxy-based negative photoresist, SU-8 (2000 series cyclopentanone-based formulation obtained from Micro Chem, MA), was electrospun to produce continuous SU-8 nanofibers to form a nonwoven fiber mesh (fabric). The process conditions needed to be optimized for this material are discussed later. Two different types of collector substrates were used to deposit these photoresist nanofibers: silicon wafers and carbon films on silicon wafers with the carbon surface treated with plasma or ultraviolet light in the presence of oxygen (UVO). For the second kind of substrate, a smooth film of SU-8 2015 (viscosity 1250 cSt) was first coated onto a Si wafer using a regular photoresist spin coater spinning at 3000 rpm for 20 s. This film
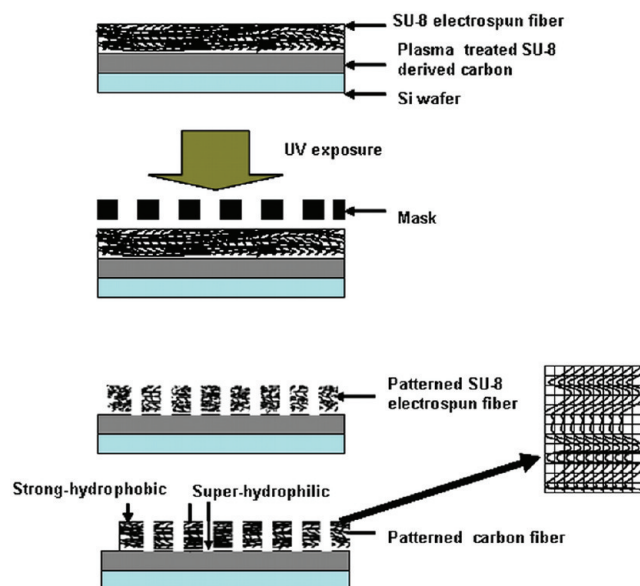

Figure 1. Schematic of the fiber patterning process. Electrospun fibers are collected on very hydrophilic plasma or a UV-treated carbon surface on a Si wafer.

was then pyrolyzed to yield a smooth carbon film using the standard C-MEMS process.[11] The substrates thus obtained were UVO or plasma treated to make the surface strongly hydrophilic.

Patterning by Photolithography and Pyrolysis. After electrospinning of the photoresist, the samples were soft baked at 95 °C for 20 min in an oven. The soft baking step is followed by lithographic patterning of the fabric surface using the SF-100 maskless lithography system from Intelligent Micro Patterning LLC, St. Petersburg, FL. This particular maskless lithography technique utilizes reflective microoptoelectromechanical (MOEM) elements to modulate light spatially with a resolution of a few micrometers over a 16 mm × 11 mm field of view. Although in the present study we have used a maskless lithography system, it is clear that any standard photolithography method can be employed to generate patterned nanofiber surfaces of the desired geometry and feature size. A schematic of the patterning process used in this study is shown in Figure 1. After UV exposure, samples are baked again at 95 °C for 20 min, and this bake is followed by the development of the patterns in a solvent (1-methoxy-2-propanol acetate, a standard SU-8 developer) for 1 min. Samples are then rinsed with isopropyl alcohol and dried in a nitrogen atmosphere. Finally, all samples are pyrolyzed at 900 °C in an inert atmosphere to yield carbon nanofibers. Before pyrolysis, the quartz tube was purged with nitrogen gas at a 0.5 L/min flow rate for about 20 min to remove unwanted air or oxygen. The heating rate was fixed at 5 °C/min, and the N_2 gas flow rate was kept constant at 0.2 L/min during heating. Once the maximum temperature was reached, it was maintained for 60 min. The furnace was then cooled to room temperature in about 10 h to obtain SU-8-derived carbon nanofibers; however, N_2 gas continued to flow to maintain the inert atmosphere.

Characterization. Field-emission scanning electron microscopy (Quanta 200, FEI, Germany; SUPRA 40 VP, Gemini, Zeiss, Germany) was used to characterize the surface morphology of the nonwoven fiber surface. The accelerating voltage was maintained at 10 kV. All samples were first sputter coated with a thin layer of Au−Pd to reduce the surface charging of the samples during electron beam scanning. The average diameter of the nanofibers was established for each sample by measuring the diameter of 50 nanofibers in 6 different fields of view and then taking their average. The wetting behavior of carbon nanofiber surfaces was characterized by measuring the static contact angle,

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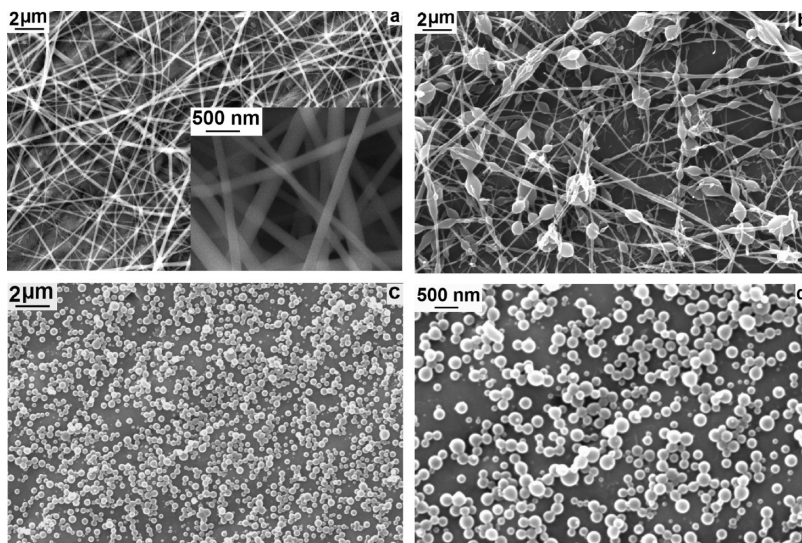
Figure 2. SEM images showing the effect of viscosity on the morphology of carbon nanofibers: (a) carbon fiber with the highest viscosity, 1250 cSt, with a high magnified view as an inset; (b) beaded fiber with medium viscosity, 140 cSt; (c) carbon nanobeads with the lowest viscosity, 7cSt; and (d) magnified view of panel c. The applied electric field strength, flow rate, and distance between source needle and collector were 2.0 kV cm^{-1}, 0.3 mL ph, and 10 cm, respectively.

and the contact angle hysteresis with a contact angle goniometer (Rame-Hart). In most of the measurements, 5 μL ($\sim$3 mm spherical drop diameter) water droplets were used.

Results and Discussion

The process for electrospinning of the SU-8 photoresist for the production of long, continuous fibers was optimized by varying the following process parameters: electric field strength, solution flow rate, and electrospinning distance. For the highest-viscosity solution, SU-8 2015 (1250 cSt), the optimized process parameters were the following: electric field, 2.0 kV/cm; electrospinning distance, 10 cm; and flow rate, 0.3 mL/h. These conditions yielded continuous ultrathin uniform fibers with an average diameter of 190 ± 40 nm (Figure 2a). As an example of this optimization, Figure 2 summarizes the role of the SU-8 viscosity/molecular weight in obtaining continuous nanofibers. Beaded fibers and beads were the only morphologies observed for the reduced-viscosity solutions of SU-8 2007 (140 cSt) and SU-8 2002 (7 cSt), respectively, while keeping other process parameters the same as detailed above. The average bead diameter varied from 820 nm for beaded fibers (Figure 2b) to 340 nm for bead-only morphology (Figure 2c,d). The failure of low-molecular-weight solutions to produce continuous fibers is related to their low viscoelasticity. At low viscosity (7 cSt), the columbic force dominates the elastic force, leading to a rapid breakup of the polymer jet (beads in Figure 2c). However, increased viscoelasticity engendered by chain entanglements does not allow the breakup of the jet, resulting in continuous fibers as shown in Figure 2a.

There is only one report[24] that we could find in which a photo-cross-linkable material was mixed with a precursor copolymer in order to photopattern polymer fibers. The present study not only allows for the direct use of an existing photoresist material for nanofiber manufacture but also allows for the conversion of the polymer fibers into conductive carbon fibers. With this approach, the patterning of fibrous surfaces over a larger area and their direct integration with other photoresist-derived structures become possible. Various patterned structures on fabric surfaces are shown in Figure 3a–f. The fabrics shown in Figure 3a–d are deposited directly onto a Si wafer, and those in Figure 3e,f are deposited onto a plasma- or UVO-treated carbon film on a Si wafer.

Figure 3a,b shows an array of microchannels photopatterned in the uniformly deposited carbon fabric. Figure 3b is a magnified view of the image shown in Figure 3a. The porous carbon nanofiber walls of these microchannels may serve as a useful element in selective adsorption and filtration in microfluidic devices. The electrical conductivity of SU-8-resist-derived carbon ($\sim$10^3 S/m) is reported to be on the order of that of glassy carbon ($\sim$10^4 S/m), a preferred electrode material in electrochemistry.[12] Thus, the patterned fibrous carbon pillar structures fabricated over a large area as shown in Figure 3c,d can be used, for example, as an array of electrodes for the formation of 3D microbatteries.[11−14] The patterned structures shown in Figure 3e,f may also be useful for immobilizing biomolecules over a specified area and thus act as passive reaction sites or as electrochemical or optical sensors. In addition, the demonstrated biocompatibility of SU-8-derived carbon[15] makes this new process for patterning nanofibrous structures suitable for use as a platform for cell culturing and tissue engineering.

Another interesting feature of patterned carbon nanofiber structures is demonstrated in the wettability results summarized in Figure 4. A smooth film of the SU-8 negative photoresist is weakly hydrophilic (water contact angle $\sim$60°), whereas the nanotextured surface made up of the carbon nanofibers in Figure 2a is very hydrophobic with a water contact angle of about 130° and contact angle hysteresis of 34°. This texture-induced hydrophobicity is similar to that observed in some electrospun polymeric nanofiber webs.[27−29] This level of hydrophobicity is quite remarkable in that it is approximately the maximum that can be obtained by texturing alone for a hydrophilic starting material, without any of the customary surface chemical modifications that are applied to nudge a material toward superhydrophobicity. In the case of a beady surface as shown in Figure 2c, the water contact angle indeed nearly approaches that of a superhydrophobic surface ($\sim$142°) with a large contact angle hysteresis of nearly 43°. This observation is consistent with the Cassie−Baxter[29] superhydrophobicity, implying that water does not penetrate

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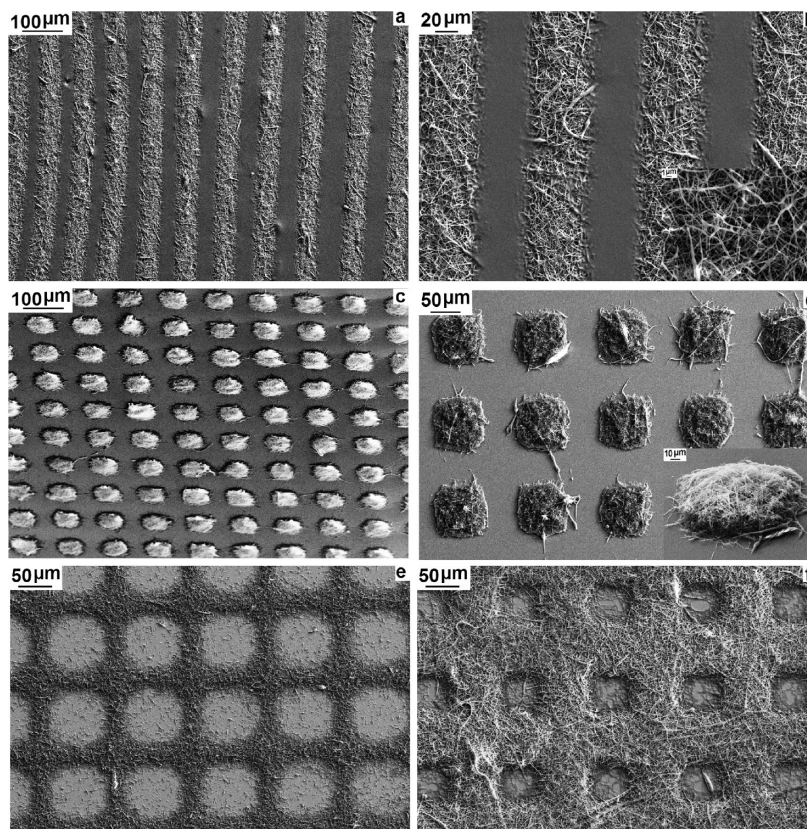(29) Ma, M.; Mao, Y.; Gupta, M.; Gleason, K. K.; Rutledge, G. C. *Macromolecules* **2005**, *38*, 9742.

Figure 3. SEM images of arrays of patterned fibrous carbon structures: (a, b) lines, (c, d) 3D pillars, and (e, f) connecting squares. Images b and d are magnified views of images a and c, respectively, and higher-magnification images of b and d are shown as insets. Images a−d are on Si wafer substrates, and images e and f are on a plasma-treated SU-8-derived carbon film on a Si wafer.
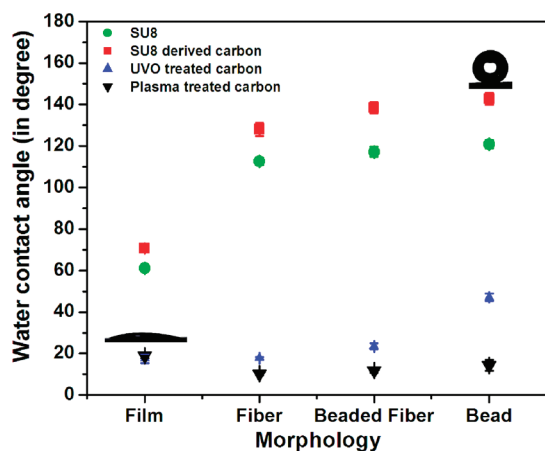

Figure 4. Effect of fiber morphology and chemical treatment on the water contact angle. Droplet images show a high water contact angle on an SU-8-derived carbon beady surface and a low contact angle on a hydrophilic plasma-treated carbon film.

the beaded fabric matrix. This phenomenon of advancing angle superhydrophobicity with a large contact angle hysteresis has been termed the petal effect.[30] Finally, a UV-ozone- or plasma-treated carbon film becomes strongly hydrophilic with a water contact angle of ∼20° (figure 4).

Clearly, patterning of carbon nanofibers as shown schematically in Figure 1 produces a strong wettability contrast between the smooth hydrophilic base and the surrounding hydrophobic nanofiber domains. This together with the facile functionalization of carbon may offer many new possibilities in microfluidics, electronic and photonic devices, biosensors, complex biomolecular reactions, selective adhesion, and the immobilization of biomaterials.[25,26,31] For example, this architecture could be employed to confine the flow of aqueous solutions to hydrophilic areas of silicon or dense carbon while partitioning hydrophobic solute/oil phases in the hydrophobic porous carbon matrix. An example of such alternating hydrophilic and hydrophobic surfaces found in nature is the structure of the Namib desert beetle's wings, which consist of an array of hydrophilic spots (about 100 μm in diameter) as surface bumps on a hydrophobic background used to collect drinking water from their fog-laden wings.[25]

Conclusion

A simple new method has been demonstrated for directly fabricating arrays of microstructures composed of carbon nanofibers on silicon and carbon substrates by photolithography. The key idea of the approach is first to produce a uniform layer of nanofibers of a sensitive photoresist, SU-8, by optimizing the electrospinning conditions and then photopattern the layer directly. SU-8 nanofibers are deposited either on silicon or on another layer of an SU-8-derived smooth carbon film. Subsequent pyrolysis yields arrays of 3D-patterned carbon nanofiber microstructures on either silicon or carbon substrates. The nanotextured surface of SU-8-derived carbon fibers is found to

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be very hydrophobic (water contact angle, $\theta \approx 130°$) without any further surface chemical treatment, whereas a smooth, dense carbon layer was hydrophilic ($\theta \approx 60°$) and can be made very hydrophilic by UV ozone or plasma treatment ($\theta \approx 20°$). These wettability and porosity contrasts offer many possibilities in microfluidic manipulations and sensors. The known electrochemical properties[12] and biocompatibility[15] of SU-8-derived glassy carbon also render these structures suitable for applications in high-surface-area electrodes for energy storage devices and bio-platforms. Our ability to directly produce and pattern nanofibrous/nanoporous layers of a widely used photoresist opens new possibilities for their integration into photolithography-based device fabrication, which has been limited thus far largely to the manipulation of dense resist layers.

Supporting Information Available: Information about the design and fabrication of the electrospinning setup used in this study and assembled in our laboratory. This material is available free of charge via the Internet at http://pubs.acs.org.