Polyelectrolyte Functionalization of Electrospun Fibers

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We report the layer-by-layer (LbL) surface functionalization of high aspect ratio (>100000:1) polystyrene (PS) electrospun fibers (ESFs) of various diameters (400 nm or 1.5 μm) with polyelectrolytes (PEs), deoxyribonucleic acid (DNA) oligonucleotides, and PE/gold nanoparticle (Au_{NP}) composite layers. ESFs were coated with poly(allylamine hydrochloride) (PAH) and poly(styrenesulfonate) (PSS) multilayers, the thickness of which was controlled by adjusting the number of PE layers deposited. PAH/PSS multilayer buildup was demonstrated by dissolving the inner PS fibers with tetrahydrofuran, resulting in the formation of hollow PAH/PSS fibers. DNA multilayer coated ESFs were also prepared using oligonucleotides with repeating blocks of adenosine and guanosine ($polyA_{15}G_{15}$) and thymidine and cytidine ($polyT_{15}C_{15}$). The $polyT_{15}C_{15}$ was labeled with tetramethylrhodamine. Linear DNA multilayer buildup on the ESFs was observed through an increase in fluorescence intensity using confocal laser scanning microscopy. Finally, nanocomposite PE/gold fibers were prepared by immersing the PAH/PSS-coated PS fibers into a dispersion of 4-(dimethylamino)pyridine-stabilized Au_{NP}. This resulted in a dense packing of Au_{NP} in the PE film localized on the PS fiber surface. These fibers have potential application in sensing, filtration, and catalysis and as release materials in medicine and agriculture.

Introduction

Electrospinning is a well-known method for obtaining polymer fibers with diameters as low as a few nanometers and length in the range of several centimeters.[1] During electrospinning, a strong electrical field is applied to a droplet of polymer solution (or polymer melt) at the tip of a capillary, which acts as one of the electrodes. The charging of the fluid leads to a conical deformation of the droplet, resulting in a thin jet.[2] As the jet solidifies, solid fibers are deposited onto the substrate in a random fashion with a deposition rate of several meters per second.[3] The process can be applied to a wide range of natural and synthetic polymers, such as polylactide, poly(vinyl acetate), poly(ethylene oxide), polyamides, or polystyrene.[4,5] The resulting electrospun fibers (ESFs) have potential applications in the fields of filtration,[6] sensing,[7] catalysis,[8] tissue engineering,[9−11] nanoreinforcement,[12,13] and protective clothing.[14,15] The high surface area-to-volume ratio of the fibers makes them suitable materials for catalysis and sensing applications. However, tailoring the surface chemistry and function of the ESFs is of utmost importance for application of these materials: for example, modification of surface properties such as chemical composition, functionality, and charge as well as biocompatibility, is essential for utilization of fibers in specific applications.

Layer-by-layer (LbL) assembly has been widely utilized over the past decade for the preparation of ultrathin surface coatings.[16] The technique involves the sequential adsorption of oppositely charged materials to construct a film in a stepwise manner. The process is commenced by adsorbing a polyelectrolyte onto an oppositely charged surface, thereby reversing the surface charge. Further layers are added by repeating the process until the desired film thickness is reached. A variety of materials can be assembled via the LbL technique, including polymers (polyelectrolytes (PEs)),[17,18]

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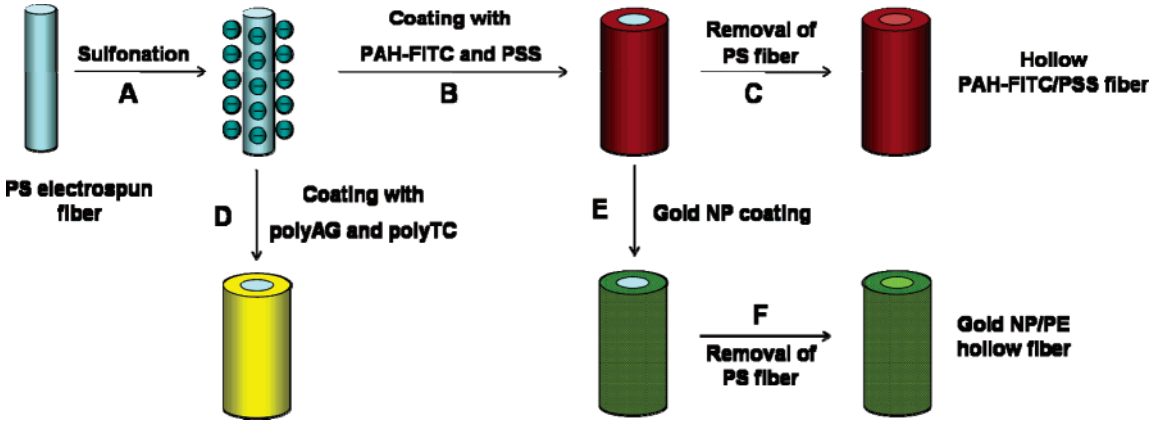
Scheme 1. Schematic Illustration of the Surface Modification of ESFs[a]



[a] (A) Treatment of ESFs with sulfuric acid to obtain a negatively charged surface. (B) LbL assembly of PAH−FITC and PSS on negatively charged fibers. (C) Dissolution of the PS ESFs with THF to obtain hollow PAH−FITC/PSS fibers. (D) DNA multilayer formation by hybridization of poly$A_{15}G_{15}$ and poly$T_{15}G_{15}$ on the ESFs. As a precursor layer PEI and polyT were initially deposited on the negatively charged PS fibers. (E) Immersion of the PE-coated PS ESFs in a DMAP−Au_{NP} dispersion to give a PE/Au_{NP} coating. (F) Au_{NP}/PE hollow fibers, obtained by dissolving the PS fibers with THF.

biomolecules,[19−21] nanoparticles,[22] and small molecules,[23] and the method can be applied to a number of different substrates, including planar supports (e.g., silicon wafer or quartz slides),[17−24] colloids,[25] carbon nanotubes,[26−29] or membranes.[30] However, the use of electrospun fiber templates for LbL coating has only found limited application thus far. Wang et al. recently demonstrated the LbL assembly of a fluorescent conjugated polymer and PAH on electrospun cellulose acetate.[7] In that study the nanofibrous membranes were used as biosensors and the quenching behavior of the sensors in aqueous solution was studied. However, in that case the LbL assembly was limited to electrostatic interactions and film thickness and morphology were not studied.

Herein, we report the surface modification of polystyrene (PS) ESFs and the subsequent preparation of PE, DNA, and PE/gold composite fibers via LbL assembly on the fiber surface. The process used for preparing these modified ESFs is illustrated in Scheme 1. There are several advantages for using such an approach. First, being based on LbL assembly, the method is applicable to a wide range of materials and allows the preparation of surface-modified fibers and fiber networks with diverse composition. In principle, the method can be generalized to include a variety of building blocks, from biomolecules to synthetic polymers and nanoparticles. Second, the length and diameter of the surface-modified fibers can be easily controlled because the ESF template properties can be readily varied during the electrospinning process. Third, the thickness of the coating can be tailored by varying the number of layers deposited. Finally, as LbL assembly is not confined to electrostatic interactions, materials can be constructed from a range of uncharged components, exploiting sequential chemical reactions,[31,32] hydrogen-bonding interactions,[33,34] or metal−ligand complexation.[35,36]

To demonstrate the applicability of LbL assembly on ESF substrates, we have used the method to coat ESFs with a range of different materials, yielding fibers with a variety of surface properties. As a model system, the well-characterized PE pair poly(allylamine hydrochloride) (PAH) and poly(styrene sulfonate) (PSS)[25,37,38] was assembled on the ESFs via the LbL technique. In this case, PAH was first labeled with fluorescein-5-isothiocyanate (FITC) to enable visualization of the fibers with fluorescence microscopy. PAH−FITC/PSS deposition on the fiber surface was further demonstrated by removal of the inner PS template, resulting in hollow PE fibers. To examine biofunctionalization of the ESFs, we also examined the buildup of biomolecule layers on the fiber surface. DNA-coated ESFs were synthesized using two diblock oligomers, one consisting of repeating units of adenosine and guanosine (poly$A_{15}G_{15}$) and the other consisting of thymidine and cytidine (poly$T_{15}C_{15}$, labeled with tetramethylrhodamine).[21] In previous work we demonstrated DNA multilayer formation on planar and colloidal supports.[21] Here, we expand this approach to fiber substrates. Unlike

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the electrostatic forces which act between oppositely charged PEs, DNA multilayer buildup is based on hybridization between the base pairs and is held together by a combination of hydrogen-bonding and hydrophobic interactions. The buildup was followed by monitoring the increase in fluorescence intensity of the coated fibers as each bilayer was deposited. Finally, we examined the functionalization of PE-coated fibers with metal nanoparticles (NPs), which may be useful in catalytic applications. PE/gold composite fibers were prepared by infiltrating PAH/PSS-coated ESFs with gold nanoparticles (Au_{NP}). Further characterization was performed using confocal laser scanning microscopy (CLSM), fluorescence microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM). Scheme 1 shows a schematic illustration of the process, with the various routes to produce PE, DNA, and PE/Au_{NP} composite fibers.

Experimental Section

Materials. Poly(styrene sulfonate, sodium salt) (PSS, M_w = 70000 g mol^{-1}), poly(allylamine hydrochloride) (PAH, M_w = 70000 g mol^{-1}), polyethylenimine (PEI, M_w = 25000 g mol^{-1}), sodium chloride, and sodium citrate were obtained from Aldrich. Polystyrene (PS, M_w = 638000 and 350000 g mol^{-1}) was provided by BASF. Oligonucleotides were custom-synthesized by Geneworks (Adelaide, South Australia). Tetrachloroauric(III) acid, sodium borohydride (98%), fluorescein-5-isothiocyanate, and tetraoctylammonium bromide were obtained from Sigma. Tetrahydrofuran (THF) and chloroform were purchased from Labscan and UniChrom, respectively. All chemicals were used as received. Fluorescein isothiocyanate-labeled PAH (PAH−FITC)[39] and 4-(dimethylamino)-pyridine-stabilized gold nanoparticles (DMAP−Au_{NP})[40] were prepared following published procedures. The water used in all experiments was passed through a Millipore Milli-Q plus 185 purification system. The buffer solution used for all DNA coatings contained 500 mM NaCl and 50 mM sodium citrate (SSC buffer).

Electrospinning of PS Fibers. The electrospinning setup has been described previously.[41] The polymer solution was pumped (using a peristaltic pump) from a reservoir through a metal capillary connected with a voltage supply. The circular orifice of the capillary had a diameter of 500 μm. ESFs with a diameter between 1 and 3 μm were spun from a 6 wt % PS solution in chloroform by using an electric field of the order of 1 kV cm^{-1}. The distance between the tip of the capillary and the counter electrode was 20 cm. The collecting target was either aluminum foil or a glass slide placed on the top of the circular counter electrode.

ESFs with a diameter of 300−500 nm were spun from a 7.5 wt % PS solution in THF with a small amount of lithium chloride (0.2 wt %). The collecting target was aluminum foil on a rotating cylinder (1500 rpm, diameter 15 cm).

Surface Modification of ESFs. Electrospun PS fibers (approximately 2 mg) were immersed into concentrated sulfuric acid (9.8 M, 2 mL) and stirred for 2 min to facilitate sulfonation of the PS surface. The entangled swollen fibers were removed from the acid solution and were subsequently washed with Milli-Q water until the solution pH was approximately 7.

Assembly of PE Multilayers on ESFs. The LbL assembly of polyelectrolytes onto PS ESFs was conducted as follows: Sulfonated PS fibers (approximately 2 mg) were immersed into an aqueous solution of PAH−FITC (0.9 mg mL^{-1}, 0.5 M NaCl) and the polyelectrolyte was allowed to adsorb for 20 min. Thereafter, the fibers were thoroughly rinsed with water for 3 min and then immersed into a solution of PSS (1 mg mL^{-1}, 0.5 M NaCl) for 20 min. After the sample was rinsed for a further 3 min, the adsorption cycle was repeated until the desired layer number was reached. Before characterization, the fibers were air-dried on a glass slide.

DNA Functionalization of ESFs. The LbL assembly of DNA diblock oligomers onto PS ESFs was conducted as follows: Sulfonated PS fibers (approximately 2 mg) were immersed into an aqueous solution of PEI (1 mg mL^{-1}, 0.5 M NaCl) for 20 min. The fibers were then thoroughly rinsed with water for 3 min, followed by immersion into a 5 μM solution of poly(thymidine) in SSC buffer for 20 min. After these two polymer layers were deposited, poly-adenosine-*block*-guanosine (poly$A_{15}G_{15}$) and poly-thymidine-*block*-cytidine (poly$T_{15}C_{15}$, labeled with tetramethylrhodamine) were alternately deposited from 5 μM solutions in SSC buffer. The deposition time was 20 min for each layer and after each deposition the sample was thoroughly rinsed with SSC buffer for 3 min.

PE/Au_{NP} Coatings on ESFs. The PE/Au_{NP}-coated fibers were prepared by adding a DMAP−Au_{NP}[40] dispersion (2 mL) to the PE-coated PS ESFs and allowing Au_{NP} adsorption to proceed for 24 h. The concentration of the DMAP−Au_{NP} dispersion was 4×10^{14} particles mL^{-1}. The PE/DMAP−Au_{NP}-coated fibers were then purified by three 1 min rinses in water.

Hollow Fiber Production. Hollow PE and PE/Au_{NP} composite fibers were prepared by immersing the coated fibers in THF (2 mL) and allowing the PS to dissolve for 24 h. The resulting hollow fibers were then purified by rinsing three times with THF (1 min each).

Instrumentation. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were recorded with a Phillips XL30 (operated at 2 kV) and Phillips CM120BioTWIN (operated at 120 kV), respectively. For fluorescence microscopy measurements, an Olympus IX71 was used. Confocal laser scanning microscope (CLSM) measurements were performed using a Leica TCS SP2 AOBS. Rhodamine 6G-, fluorescein-5-isothiocyanate-, and tetramethylrhodamine-coated fibers required excitation wavelengths of 543, 488, and 405 nm, respectively. Images were recorded with a lateral and axial resolution of 170 and 350 nm, respectively. For analysis the software Imaris (Bitplane^{AG}) V.4.2 was used. For quantitative measurements of the film buildup, a pulsed picosecond diode laser (405 nm) was used instead of a continuous wave laser. This laser has a peak power of >300 mW, which ensures that all of the fluorophores are excited with each pulse.

Results and Discussion

Preparation of PS ESFs and Surface Modification. High molecular weight PS fibers with an average diameter of either 400 nm or 1.5 μm and aspect ratios of higher than 100000:1 were prepared by electrospinning. The fiber samples were collected onto aluminum foil from where the fiber mat was easily removed using tweezers. PS was chosen as the fiber material because of its well-known solubility in organic solvents, its resistance to water, and the ease of chemically modifying the polymer. To produce a strong interaction between the first PE layer and the PS surface, the ESFs were chemically modified to impart a charge to the surface. Sulfonation of phenyl groups is a well-known reaction and

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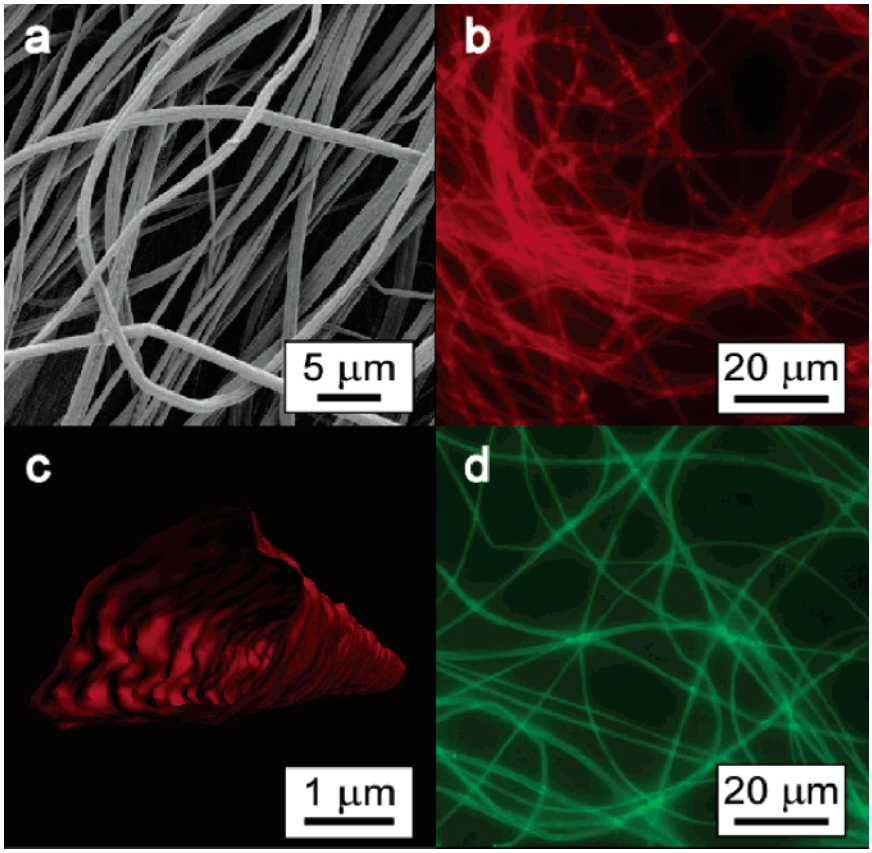

Figure 1. (a) SEM image of electrospun PS fibers after treatment with sulfuric acid and air-drying. The surface appears similar to untreated fibers (not shown). (b) Fluorescence microscopy image of rhodamine 6G-coated electrospun PS fibers. (c) 3D CLSM image of rhodamine 6G-coated electrospun PS fibers confirms the surface modification with sulfuric acid. (d) Fluorescence microscopy image of ESFs coated with PAH−FITC, confirming the uniform coating of PAH−FITC.

was demonstrated on PS by Siqueira-Petri et al.[42] We accomplished the partial sulfonation of the PS phenyl groups by treating the ESFs with concentrated sulfuric acid (9.8 M) for 2 min, yielding a negatively charged surface (Scheme 1, step A). During the sulfonation process, increased swelling of the fibers was observed, which indicates the presence of a water-swollen region of sulfonated PS at the surface of the fiber. An SEM image of the sulfonated PS ESFs is shown in Figure 1a.

Further support for sulfonation was obtained by adsorption of rhodamine 6G onto the fiber surface. At low pH rhodamine 6G is positively charged and should therefore interact electrostatically with the negatively charged fibers, binding to the fiber surface. The sulfuric acid-treated fibers were immersed into the dye, rinsed, and imaged using CLSM and optical fluorescence microscopy. The dyed fibers showed strong fluorescence (Figure 1b) compared with nonsulfonated fibers (data not shown). This confirms that treatment with sulfuric acid resulted in a negatively charged surface. Figure 1c shows a 3D cross section of a single fiber obtained by CLSM. The binding of rhodamine 6G is localized near the fiber surface. Therefore, it can be assumed that the sulfonation reaction is confined to the phenyl groups closer to the fiber surface. Complete sulfonation of the bulk material can be ruled because the fibers remained insoluble in water. However, after sulfonation the fibers swell in water, indicating increased hydrophilicity of a PS domain close to the fiber surface. SEM images showed no discernible difference in the surface morphology of the fibers after sulfonation (Figure 1a).

PAH−FITC/PSS Fibers. Layer-by-layer assembly on ESFs was first performed using PAH and PSS (Scheme 1, step B), which interact predominantly by electrostatic forces. In each layering cycle, the fibers were exposed to the PE for 20 min, followed by copious rinsing with water. To confirm the adsorption of PAH onto the sulfonated fiber surface, PAH was first labeled with the fluorescent dye flourescein-5-isothiocyanate (FITC). Figure 1d shows a fluorescence microscopy image of PS fibers coated with one layer of PAH−FITC. Strong fluorescence confirms that PAH−FITC is adsorbed onto the fibers. Multilayer assembly was then continued, alternating between the negatively charged PSS and the positively charged PAH. A comparison of SEM images of PS fibers before and after PE multilayer assembly reveals a dramatic change in the surface morphology for the PE layered fibers (Figures 1a and 2a). The surface roughness increased considerably after the adsorption of five bilayers of PAH−FITC/PSS. The increased roughness can be rationalized by the swelling behavior of the sulfonated fibers in aqueous solution. Multilayer growth takes place on the swollen fibers, and therefore drying the multilayer-coated fibers leads to shrinkage of the coating, and thus the increased surface roughness. To confirm PE deposition on the fiber surface, the multilayered fibers were exposed to THF, resulting in dissolution of the PS substrate and yielding

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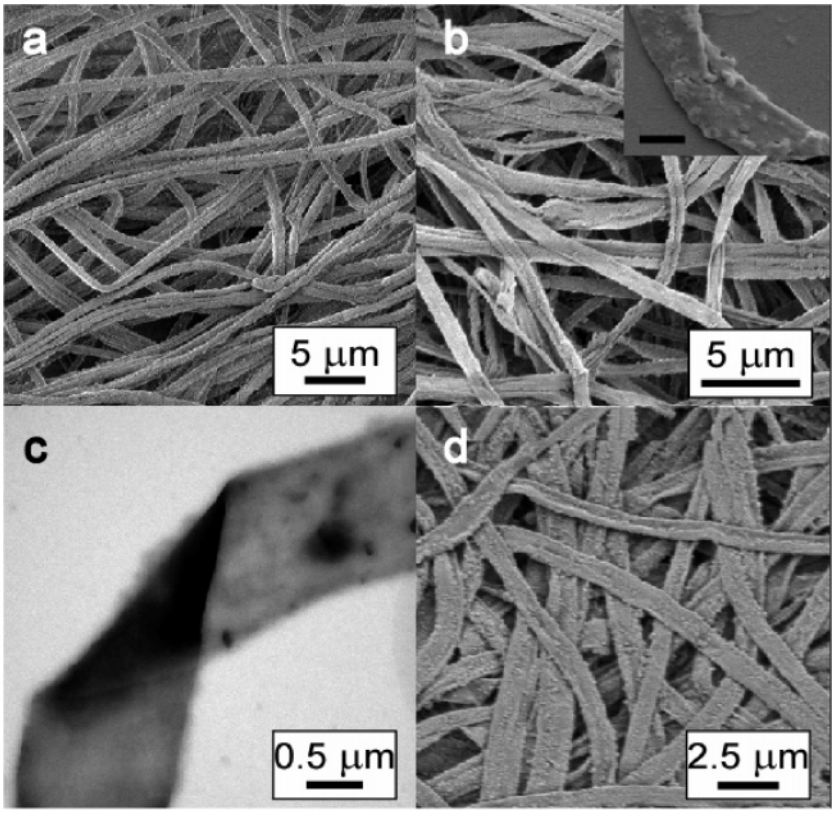

Figure 2. (a) SEM image of ESFs coated with five bilayers of PAH−FITC/PSS. (b) SEM image of hollow PAH−FITC/PSS fibers (five bilayers) after dissolving the inner PS fiber. Inset: The collapsed hollow PE fiber shows a folded structure and high surface roughness. The scale bar corresponds to 500 nm. (c) TEM image of a collapsed and folded hollow PAH−FITC/PSS fiber (five bilayers). Black dots indicate some remaining PS from the ESF template. (d) SEM image of collapsed hollow PAH−FITC/PSS fibers with ten bilayers after dissolving the inner PS fiber.

hollow PE fibers (Scheme 1, step C). Dissolved PS was removed from the THF supernatant, indicating successful dissolution of the original fibers. SEM images of the resulting hollow PE fibers are shown in Figure 2b. After removal of fibers and air-drying, the tubular structure collapses, resulting in flat hollow "ribbons". Similar behavior is also observed for hollow PE capsules, which "deflate" upon drying.[25,43] Tapping mode AFM measurements confirm the collapsed structure of the hollow fibers (data not shown). Further, by examining the apparent height of an air-dried PAH−FITC/PSS hollow fiber with AFM, it is possible to estimate the thickness of the multilayer coating. By this method the height of a five-bilayer PAH−FITC/PSS collapsed hollow fiber was determined to be approximately 110 nm (i.e., a wall thickness of 55 nm, an average layer thickness of 5.5 nm). This is considerably thicker than expected from previous studies of PAH/PSS multilayers, where a thickness of ∼2 nm per layer has been reported.[25,37,44] The comparatively higher thickness of the PE hollow fibers observed in this case is most likely due to sulfonation of the ESFs, giving a brushlike layer of sulfonated PS on the fiber surface. This brushlike layer may facilitate the adsorption of higher amounts of material, and therefore yield a higher total thickness.[45] This is consistent with the swelling observed for the sulfonated ESFs, which indicates a reasonably thick layer of sulfonated material near the fiber surface.

A TEM image of a hollow PE fiber is shown in Figure 2c. This image also shows the flat structure observed with AFM and SEM, and the flexibility of the hollow fibers is demonstrated by the ability of the fibers to fold at certain points. Small dark areas and dots in the image indicate some remaining undissolved PS, which may also contribute to the higher-than-expected thickness measured using AFM.

Similar ESFs coated with 10 bilayers of PAH−FITC/PSS also resulted in hollow fibers (Figure 2d). AFM studies on these fibers revealed an average height of approximately 140 nm (wall thickness of 70 nm, data not shown). Therefore, the addition of five extra bilayers leads to an increase in the wall thickness of 15 nm. From this difference it is possible to estimate an individual layer thickness of approximately 1.5 nm, which is consistent with literature values.[25,37,44] This also supports the argument that the higher overall thickness is attributable to a thicker precursor brush of sulfonated PS. From that data, it is clear that the wall thickness is dependent on the number of bilayers adsorbed and can therefore be tailored by the number of LbL deposition steps.

DNA-Coated PS ESFs. Recently, we published the multilayer buildup of DNA on planar and colloidal supports based on DNA hybridization.[21] Using electrospun PS fibers with an average diameter of 400 nm and an aspect ratio of at least 100000:1 as a fibrous substrate, we were also able to assemble diblock oligonucleotides (poly$A_{15}G_{15}$ and poly$T_{15}C_{15}$) on the ESFs. The fibers were first treated with sulfuric acid (as described earlier) to impart an initial charge

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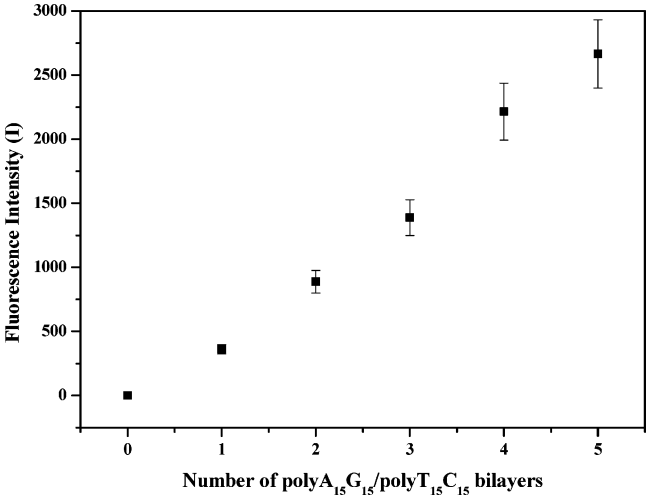

Figure 3. Fluorescence intensity as a function of bilayer number (polyAG/polyTC) deposited on electrospun PS ESFs. PolyTC was labeled with the fluorescent dye teramethylrhodamine. The fluorescence intensity was measured after each deposition of polyTC by CLSM.

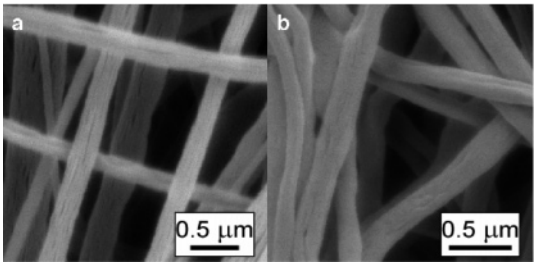

Figure 4. (a) SEM image of PS ESFs before coating with polyAG and polyTC. Small pores are evident in the fiber structure originating from the electrospinning process. (b) SEM image of ESFs coated with five bilayers of polyAG/polyTC. The surface is smooth compared with Figure 2a.

to the surface. Then, to facilitate electrostatic adsorption of the negatively charged DNA layers, a positively charged layer of PEI was adsorbed on the fibers. This PEI layer enabled a primer layer of poly-thymidine (polyT) to be electrostatically deposited on the surface. PolyT is adsorbed first to ensure that when the $polyA_{15}G_{15}$ is introduced, hybridization occurs between the polyA region of the oligomer and the polyT on the surface. This leaves the polyG domain free to hybridize with the polyC domain of $polyT_{15}C_{15}$. Multilayer DNA buildup was then accomplished by adsorbing $polyA_{15}G_{15}$ and $polyT_{15}C_{15}$, (labeled with tetramethylrhodamine) in an alternating manner (Scheme 1, step D). After each polynucleotide deposition (20 min), the fiber sample was rinsed with SSC buffer. The multilayer buildup was followed by measuring the fluorescence intensity of the DNA-coated fiber sample by CLSM after the deposition of each bilayer ($polyA_{15}G_{15}/polyT_{15}C_{15}$). Figure 3 shows a linear increase in fluorescence intensity with increasing bilayer number, reflecting linear DNA multilayer growth on the electrospun PS fibers. These results are consistent with our previous studies on the buildup of DNA multilayers on planar supports.[21] Comparison between untreated PS fibers and DNA-coated fibers in Figures 4a and 4b reveals a smooth surface coating of DNA. Small pores, which are evident on the PS fibers in Figure 4a, originate from the electrospinning process and are mostly covered by the DNA layers (Figure 4b). The smooth surface of the DNA-coated PS fibers compared with the relatively rough surface of the PAH/PSS-coated fibers in Figure 2a may be ascribed to the initial PEI coating and the DNA multilayer itself, which lead to a smoothing of the surface. Removal of the inner PS fiber to obtain hollow DNA fibers was not possible, as disassembly of the DNA multilayer takes place in THF.

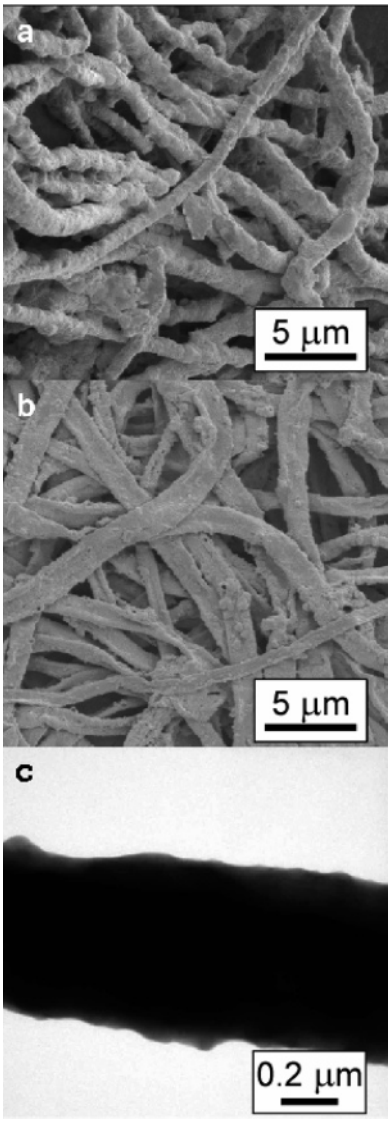

Figure 5. (a) SEM image of $(PAH-FITC/PSS)_5$-coated PS ESFs after immersion into a DMAP−Au_{NP} dispersion. The Au_{NP} infiltrate the PE coating and lead to a dense Au_{NP} packing. (b) SEM image of hollow $(PAH-FITC/PSS)_5/Au_{NP}$ composite fibers. The fiber structure collapses after dissolving the inner PS fiber in THF. (c) TEM image of a hollow $(PAH-FITC/PSS)_5/Au_{NP}$ composite fiber, showing the dense Au_{NP} packing.

PE/Au_{NP}-Functionalized ESFs. Surface modification of the ESFs was achieved by exploiting Au_{NP} self-assembly onto PAH/PSS-coated fibers. Using this approach, it is possible to obtain a dense Au_{NP} packing on the surface of the fibers. To this end, we exposed PAH−FITC/PSS-coated ESFs to a dispersion of DMAP−Au_{NP} (diameter = 6 nm) for 24 h (Scheme 1, step E). These nanoparticles have previously been shown to yield a homogeneous Au_{NP} coating in PAH/PSS multilayer films.[46] One important advantage of using DMAP−Au_{NP} is that, unlike covalently attached ligands (such as thiols), the DMAP ligand can be removed by washing with

(46) Gittins, D. I.; Susha, A. S.; Schoeler, B.; Caruso, F. *Adv. Mater.* **2002**, *14*, 508.

water. This is useful in fields such as catalysis, where the purity of the metals is important for the catalyst activity. Figure 5a shows an image of the air-dried PE fibers with a dense Au_{NP} coating. The fibers appear noticeably rougher than those coated only with PAH−FITC/PSS. Dissolution of the PS core was again achieved by exposing the gold fibers to THF (Scheme 1, step F). SEM (Figure 5b) reveals that after PS removal and air-drying the hollow PE/Au_{NP} fibers collapse, as observed for the hollow PE fibers. The dense Au_{NP} packing on the fibers was visualized by TEM (Figure 5c), which indicates a low transmission of incident electrons through the film. Further, tapping mode AFM measurements indicated a height of approximately 200 nm for the collapsed hollow PE/Au_{NP} fibers (data not shown). This is close to double that observed for the pure PE hollow fibers (110 nm), indicating that the incorporation of Au_{NP} into the fiber coating leads to a considerable increase in the thickness of the coating. Such dramatic thickness variation may also result in changes to the mechanical properties of the modified ESFs.

Conclusions

The electrospinning process offers a wide range of possibilities for tailoring the size, orientation, and composition of fibers that can be subsequently modified using the LbL technique. We have demonstrated that ESFs can be readily modified by the LbL assembly of synthetic polymers (such as PAH−FITC and PSS) or by biopolymers such as DNA. This allows tailoring of the surface properties for potential applications in filtration, sensing, and medical devices. When the inner PS fiber is dissolved, hollow PE fibers can also be synthesized. These hollow PE fibers indicate the homogeneity and integrity of the fiber coating. Furthermore, it is possible to infiltrate nanoparticles into the PE-coated fibers to prepare PE/Au_{NP} composite and hollow fibers, which may find use in fields such as catalysis and material reinforcement.

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