

Controlling the Deposition of Light-Emitting Nanofibers/Microfibers by the Electrospinning of a Poly(*p*-phenylene vinylene) Polyelectrolyte Precursor

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Received 13 April 2008; accepted 4 May 2009

DOI 10.1002/app.30686

Published online 24 June 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Poly(*p*-phenylene vinylene) (PPV) nanofibers with disordered, helical, and yarn morphologies were controllably prepared by the electrospinning of a cationic polyelectrolyte precursor in an ethanol solution followed by thermal conversion. Through the tuning of the precursor solution properties and processing variables, the factors affecting the morphology of PPV fibers were studied. The diameter of these PPV nanofibers decreased with a decrease in the precursor concentration, and gradual

blueshifts and changes in the relative intensity of the vibronic components in photoluminescence spectra were observed. These nanofibers with excellent fluorescent properties are potentially interesting for many applications such as micro- and nano-optoelectronic devices and systems. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1864–1869, 2009

Key words: conjugated polymers; fibers; fluorescence

INTRODUCTION

Electrospinning is a convenient technique for converting a polymer solution into polymeric nanofibers.^{1–3} A wide variety of polymers, including natural and conjugated polymers, have been electrospun into nanoscale- or microscale-diameter fibers with electrospinning.^{4,5} In the electrospinning process, a polymer solution is charged with a high electrical voltage. The charged electrospinning jet follows nearly straight electric field lines for a certain distance away from the tip, and then the jet bends and develops a series of lateral excursions that grow into spiraling loops. Each of these loops grows larger in diameter as the jet grows longer and becomes thinner, and then the jet solidifies because of the rapid solvent evaporation and deposits on the collector as a disordered continuous filament.^{6,7}

Many neutral polymers have been electrospun in recent years. In contrast, there has been significantly less work focused on electrospinning polyelectro-

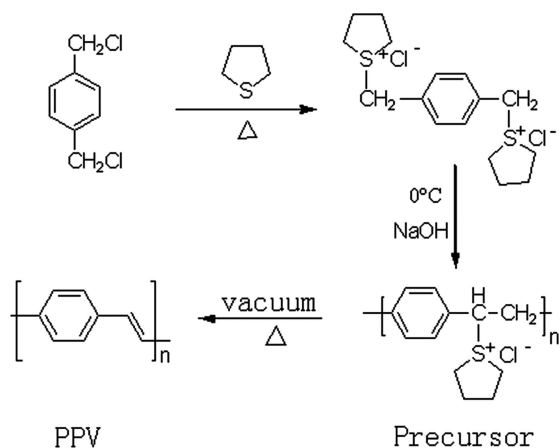
lytes and especially cationic polyelectrolytes. Unlike proton-conducting polyelectrolytes such as poly(acrylic acid),^{8,9} a charge is present on each repeating unit of a cationic polyelectrolyte. Therefore, the charged cationic polyelectrolyte jets may undergo more complex instability than neutral polymers during electrospinning.^{10,11}

Poly(*p*-phenylene vinylene) (PPV), as a conjugated polymer, is known to exhibit excellent photoluminescence (PL) and electroluminescence,¹² photovoltaic properties,¹³ and nonlinear optical properties.¹⁴ Optical nanodevices fabricated with one-dimensional PPV nanostructures may be advantageous in light-emitting diodes and photonic applications, such as wave guidance and all-optical switching. However, PPV is difficult to process because of its insolubility and infusibility. One strategy for solving this problem is to process a soluble sulfonium precursor of PPV (a cationic polyelectrolyte) and then convert the resulting objects into PPV by thermal conversion.^{15,16} Until now, most reported light-emitting electrospun fibers have been prepared from composite solutions consisting of functional materials and matrix polymers.^{17–21} However, PPV can be prepared as emitting electrospun fibers from a pure precursor solution. Because of the diverse potential applications of PPV nanostructures, it is desirable to fabricate pure PPV into various morphologies of nanoscale dimensions, and this may be advantageous for both fundamental research and practical applications. Herein we report

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Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 20774017 and 20872030.

Contract grant sponsor: Analysis and Testing Foundation of Northeast Normal University.



Scheme 1 Synthesis route of PPV.

that light-emitting fibers with disordered, helical, and yarn morphology were prepared by the electrospinning of a PPV polyelectrolyte precursor in an ethanol solution.

EXPERIMENTAL

Materials

p-Xylylene dichloride (98%) and tetrahydrothiophene (98%), purchased from Aldrich Chemical Co. (Milwaukee, WI) were used to prepare the PPV precursor. The ethanol was reagent-grade. These chemicals were used without further purification. The PPV precursor polymer was synthesized according to the

standard polyelectrolyte route²² and dialyzed against ethanol for 3 days. Then, the precursor, a poly(xylylidene tetrahydrothiophenium chloride) ethanol solution, was obtained. The process is presented in Scheme 1. The weight ratio of the solvents was 95/5 (ethanol/water), and this was detected with gas chromatography spectrometers with a flame ionization detector.

Preparation of the PPV fiber samples

PPV precursor solutions with different concentrations (precursor concentration = 0.4, 0.8, 1.2, 1.6, or 2.0 wt %) were prepared for electrospinning. The electrospinning device consisted of a capillary (tip diameter = 0.6 mm), which included a wire electrode, a grounded collector, and a high-voltage power supply. The electrospinning was conducted at room temperature and at a relative humidity of about 30%. The flow rate of the polymer solution was equal to 1 mL/h. The operating voltage was varied from 10.5 to 17 kV. Electrospun PPV precursor nanofibers were collected on grounded aluminum foil or a grounded indium tin oxide substrate with a small piece of insulating glass on it, which was placed 25 cm below the capillary tip. PPV films were prepared on the quartz substrate by spin coating. The films and electrospun fibers were heated at 210°C for 6 h in a vacuum oven for the conversion of the precursor into PPV.

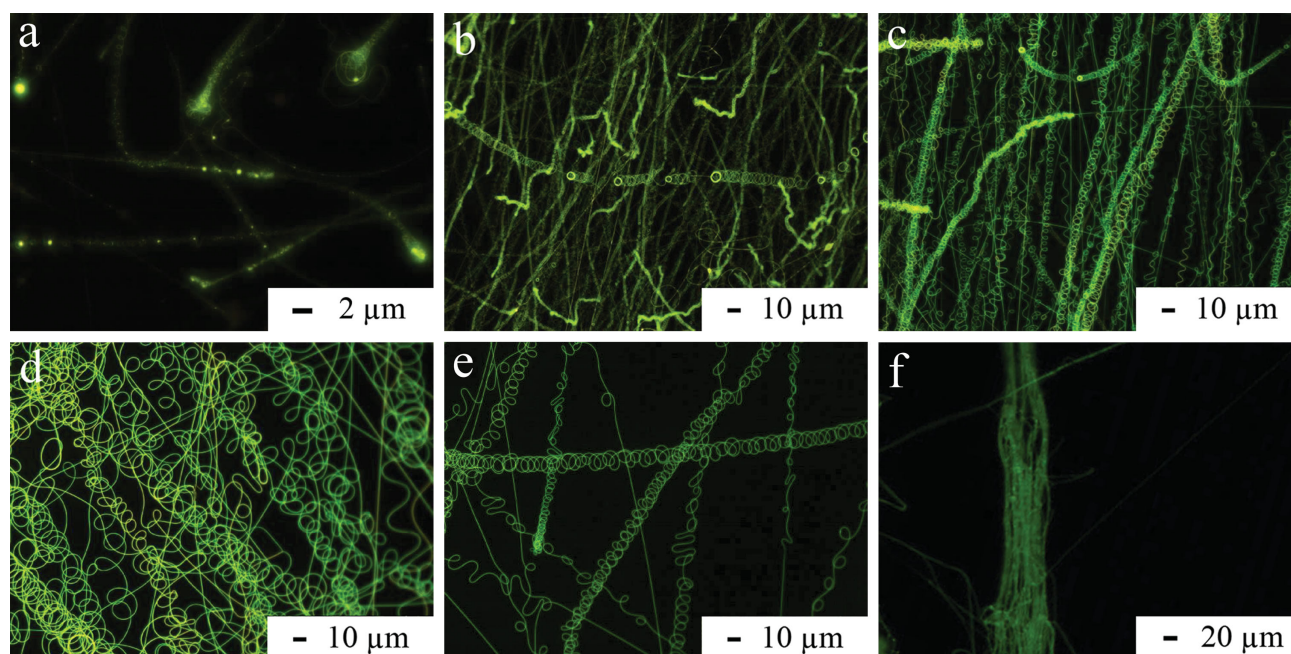


Figure 1 Fluorescence microscopy images of (a–d,f) PPV fibers with a precursor concentration of 0.4, 0.8, 1.2, 1.6, or 2.0 wt % (collecting time = 1 min) and (e) fibers with a precursor concentration of 1.6 wt % (collecting time = 30 s). All the fiber samples were electrospun under 12 kV. The helices were collected directly by the grounded substrate. The fiber yarns were collected with a glass slide to cross through the gap between the electrospinning capillary tip and grounded collector surface. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

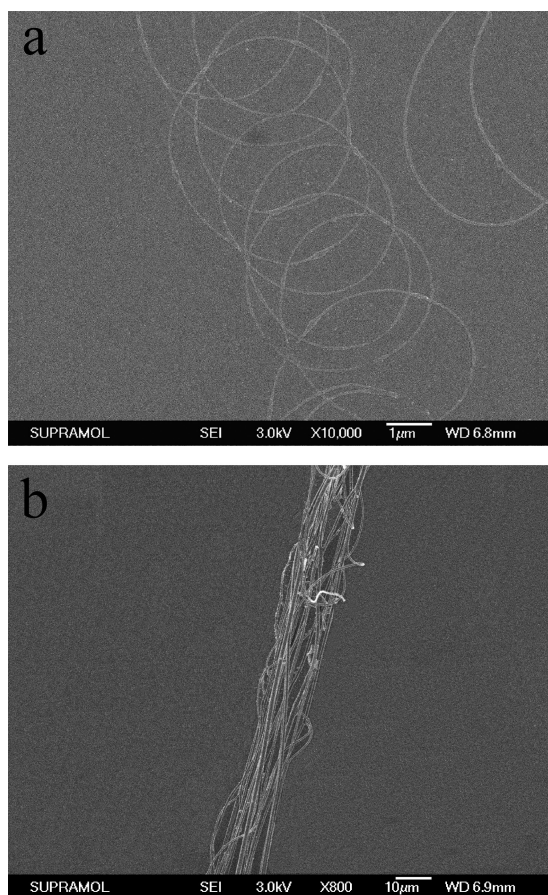


Figure 2 SEM images of typical PPV (a) helices and (b) yarns.

Characterization of the electrospinning solutions and fiber samples

All the fiber samples were observed with fluorescence microscopy (TE2000-U, Nikon, Tokyo, Japan) and scanning electron microscopy (SEM; S-570, Hitachi Corp., Japan). PL spectra were taken on an HR-800 LabRam confocal Raman microscope (JY Co., France) with excitation by a continuous He–Cd laser at the wavelength of 325 nm. Fourier transform infrared (FTIR) spectra were obtained on a Magna 560 FTIR spectrometer (Nicolet Corp., United States).

RESULTS AND DISCUSSIONS

Morphologies of the electrospun PPV samples with different precursor concentrations

Figure 1 shows the fluorescence microscopy images of PPV nanofibers prepared from PPV precursor solutions with different concentrations. These fibers were electrospun at a fixed voltage of 12 kV. Unexpected helical and yarn morphologies were observed. Figure 1(a) shows the fibers electrospun from the 0.4 wt % PPV precursor. They consisted of helical

structures with bead-on-string morphology, and no linear fibers were observed. As the precursor concentration was increased to 0.8 wt %, the collected fibers consisted of helical structures without beads [Fig. 1(b)]. With the concentration increased to 1.2 and 1.6 wt %, the collected fibers consisted of helical and linear structures [Fig. 1(c,d)]. All these fiber samples were collected for 1 min. Figure 1(e) shows the PPV fibers with the precursor concentration of 1.6 wt % that were collected for 30 s. The morphology of these PPV fibers [Fig. 1(e)] was similar to that of the fibers collected for 1 min [Fig. 1(d)], and this suggests that the influence of the collecting time on the morphology of the PV fibers could be neglected. When the concentration of the PPV precursor was up to 2.0 wt %, no helical structures were observed, and the solution was electrospun into yarns perpendicularly on the surface of the conductive collector [Fig. 1(e)]. SEM images of typical PPV helices and yarns are shown in Figure 2(a,b).

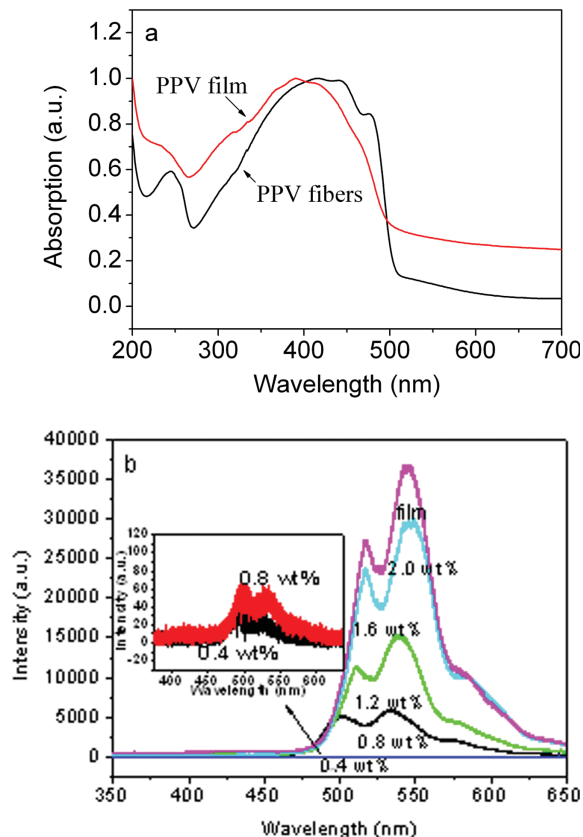


Figure 3 (a) Ultraviolet–visible absorption of PPV fibers electrospun from a 1.2 wt % precursor solution and a PPV film and (b) PL spectra of PPV fibers (only one fiber in the focused region) electrospun from precursor solutions with different concentrations and a PPV film. The inset shows the details of PL spectra of PPV fibers with a precursor concentration of 0.4 or 0.8 wt %. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

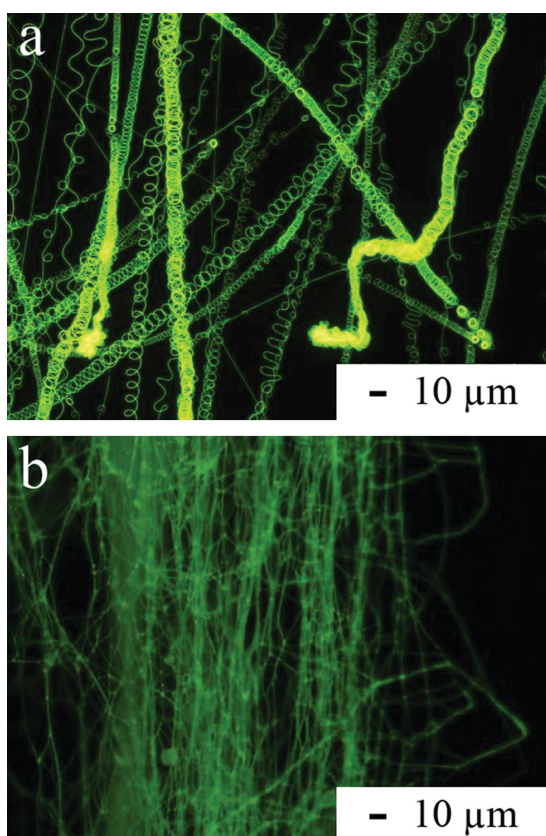


Figure 4 PPV fibers electrospun with a precursor concentration of 1.2 wt % under (a) 10.5 and (b) 17 kV. The helices were collected directly by the grounded substrate. The fiber yarns were collected with a glass slide to cross through the gap between the electrospinning capillary tip and grounded substrate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Investigation of the photophysical properties

The photophysical properties of these PPV fibers and film were investigated with ultraviolet–visible and PL spectroscopy. As shown in Figure 3(a), absorption bands at about 400 nm were observed, and they were attributed to the π - π^* transition of the PPV component. The absorption peak of PPV fibers was slightly broader than the peak of the PPV film and shifted to a higher energy level. Figure 3(b) shows the PL emission spectra of the PPV fibers and film. These PPV samples emitted yellow-green fluorescence at about 550 nm with two vibronic sidebands, which were assigned to 0–1, 0–0, and 0–2 transitions.²³ The emission peak that originated from the 0–0 transition of these fibers was observed at 517, 510, 502, 499, and 483 nm as the concentration of the PPV precursor decreased from 2 to 0.4 wt %. The blueshifts in the PL spectra were also observed when the thickness of the PPV film decreased, and this was attributed to the decrease in reabsorption.²⁴ In these PPV fibers, the diameters of the fibers

decreased with the decrease in the concentration of the PPV precursor (Fig. 1). Therefore, these blueshifts may be attributed to reduced reabsorption by neighboring chains of the emitted light that originated from the 0–0 transition because the thin fibers consisted of fewer polymer chains in comparison with the thick fibers and also to much fewer inter-chain contacts between the polymer chains. In addition, with the concentration of the PPV precursor decreasing from 2 to 0.4 wt %, the 0–0 peak was enhanced and the 0–1 peak was gradually reduced in the PL spectra. This change in the relative intensity of the vibronic components in the PL spectra of the PPV fibers can also be explained from the viewpoint of reabsorption. The blueshift and change in the relative intensity of the vibrant components in the PL spectrum were also observed in a comparison of the spectrum of the PPV fibers with that of the PPV bulk film.

Effects of the processing variables on the morphologies of the PPV fibers

Another factor that affected the morphology of the PPV fibers was the operating voltage. As shown in

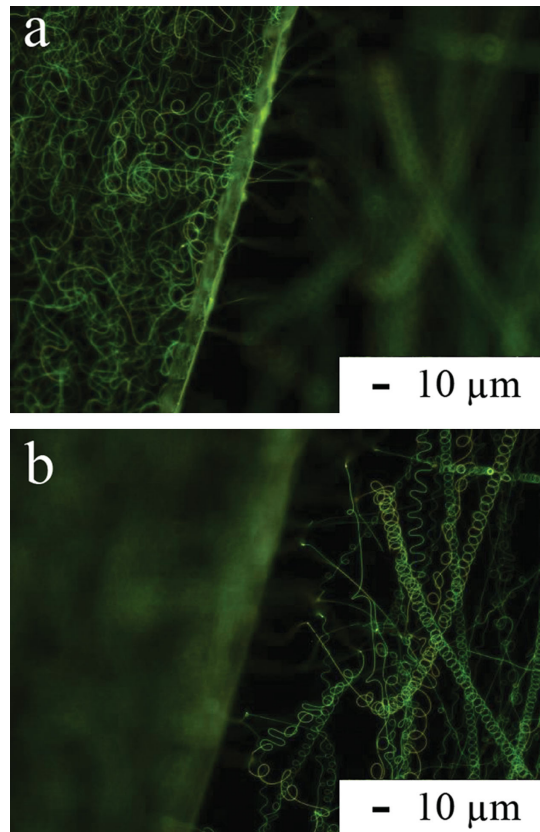


Figure 5 PPV fibers deposited onto (a) an insulating plate and (b) a grounded substrate. The electrospinning voltage was 12 kV. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figures 4(a), 1(c), and 4(b), the PPV fibers electrospun with a precursor concentration of 1.2 wt % under voltages of 10.5, 12, and 17 kV exhibited different morphologies. All the fibers were collected for 1 min. The amount of fibers electrospun under 10.5 kV was less than the amount of fibers electrospun under 12 kV [Figs. 4(a) and 1(c)]. This can be explained by the enhancement of the spinning rate due to the increase in the operating voltage. When the voltage was up to 17 kV, the fibers were ejected rapidly and spontaneously electrospun into yarns perpendicularly to the surface of the conductive collector [Fig. 4(b)]; this was similar to what is shown in Figure 1(e) for electrospinning the precursor with a concentration of 2 wt % and an operating voltage of 12 kV.

The kinds of collectors also affected the morphology of the electrospun PPV fibers. Figure 5 shows the PPV fibers collected by a grounded substrate with a small piece of an insulating plate on it. The electrospinning voltage was 12 kV. We can see that the fibers deposited on the insulating plate were disordered [Fig. 5(a)]; however, the fibers deposited on the grounded substrate had a helical morphology [Fig. 5(b)].

FTIR spectroscopy investigation

Figures 6 and 7 show the FTIR spectra of PPV nanofibers electrospun with different precursor concentrations and processing variables. The FTIR spectrum of the PPV film is shown also. The characteristic absorption peaks of the PPV fibers appear at 961 [*trans*-vinylene δ (C–H stretching) out-of-plane mode], 1200 [vinylene γ (C–H stretching) in-plane mode], and 2930 cm^{-1} [*trans*-vinylene δ (C–H stretching) mode].²⁵ The results indicate that these

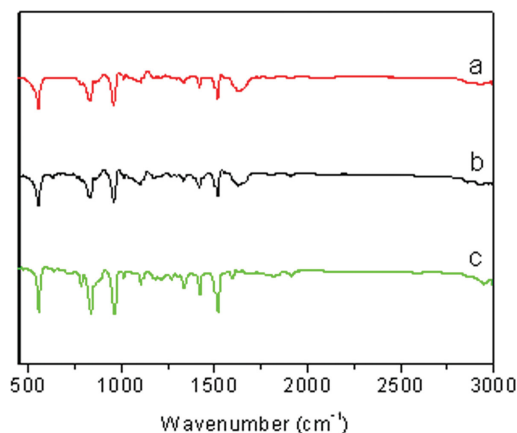


Figure 6 FTIR spectra recorded in the range of 400–3000 cm^{-1} for (a,b) PPV fibers electrospun with a precursor concentration of 0.4 or 2.0 wt %, respectively, and (c) a PPV film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

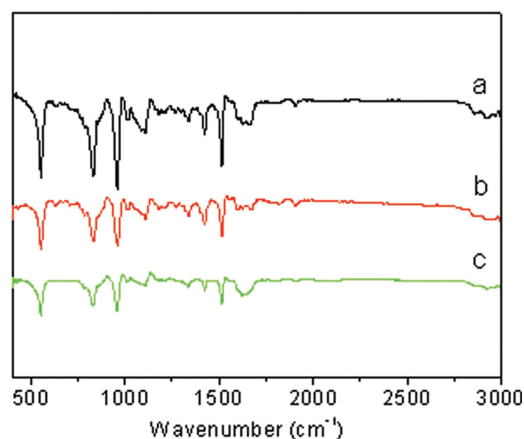


Figure 7 FTIR spectra recorded in the range of 400–3000 cm^{-1} for PPV fibers electrospun with a precursor concentration of 1.2 wt % under (a) 12 (the fibers were collected by an insulating plate), (b) 17 (the fibers were collected by a grounded substrate), and (c) 12 kV (the fibers were collected by a grounded substrate). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

fiber samples were pure PPV nanofibers and that the main structures of PPV were not changed in these fibers with various morphologies. They also suggest that the electrospinning process did not influence the composition.

CONCLUSIONS

PPV precursor solutions were successfully electrospun into nanofibers with diverse disordered, helical, and yarn morphologies through the control of the precursor concentration, operating voltage, and collector type. Regular helical PPV fibers were obtained from the electrospinning of 0.4, 0.8, 1.2, and 1.6 wt % cationic polyelectrolyte precursor solutions. These helices with uniform coils are promising templates for generating various inorganic helices with potential applications in sensors, transducers, resonators, and photonics. When the concentration of the precursor or the operating voltage was much higher, PPV precursor yarns were collected by a conductive target. The PL spectra of these PPV fibers showed a blueshift and a change in the relative intensity of the vibronic components with a decrease in the fiber diameter.

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