Highlighting the novelty of the work: Ionic-liquid-doped PEDOT twisted fibers exhibit a higher conductivity and show a repeatable cycle loop of tensile-resilience.

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ARTICLE

Twisted microropes for stretchable devices based on electrospun conducting polymer fibers doped with ionic liquid

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We report an effective method to fabricate poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate)-polyvinyl pyrrolidone (PEDOT:PSS-PVP) fiber arrays doped with ionic liquid (IL). Then twisted microropes were obtained by twisting the electrospun aligned polymer fiber arrays. It was found that the twisted rope exhibited higher electrical conductivity ($\sim 1.8 \times 10^{-4}$ S cm^{-1}) after IL doping (1.96 wt%) than those without doping ($\sim 0.8 \times 10^{-5}$ S cm^{-1}), and its conductivity was linear correlation with strain up to 35% (which is one magnitude larger than previous reports) and showed repeatable cycle loop of tensile-resilience. The extensible rate could reach up to more than 90%, much higher than that of ropes without IL doping ($\sim 17\%$). The results indicate that the twisted PEDOT:PSS-PVP ropes may be used as elastic semiconductors and stretchable sensors.

1 Introduction

Conducting polymers (CPs) have attracted much attention because of their unique physical and chemical properties, as well as their widely potential applications.[1] Poly(3,4-ethylenedioxythiophene) (PEDOT) was first synthesized by German Bayer company in 1991.[2,3] Many publications reported that PEDOT composites doped with highly polar solvents have higher electrical conductivity.[4] For instance, Dimitriev *et al.* have fabricated PEDOT:PSS films with higher conductivity by doping with ethylene glycol or dimethyl sulfoxide.[5,6] Electrospinning is an effective way for fabrication of continuous ultrafine fibers, and has gained great interest in producing filaments of functional polymers.[7-9] Owing to poor solubility in most of solvents, ultrathin CP fibers are not easy to prepare directly by electrospinning. Usually, two strategies are employed: (a) Using other spinnable polymer fibers via electrospinning as templates, CP is deposited on the template fibers by *in situ* polymerization, and then CP composite fibers are obtained.[10,11] (b) Through adding some other spinnable polymers such as polyethylene oxide (PEO) and polymethylmethacrylate (PMMA) to increase viscosity, a composite CP solution can be electrospun into nanofibers directly, but the thickener added usually reduces the electrical conductivity of the composite CP fibers obviously.[12-15] For example, Sun *et al.* have fabricated tensile sensors by

electrospining PEDOT:PSS-PVP nanofibers.[16] However, the room-temperature conductivity of the composite fibers was only 1.6×10^{-5} S cm^{-1}, which is much lower than some other conductive materials such as metal nanowires or carbon nanotubes.[17-19]

Ionic liquids (ILs), composed of cation and anion, are organic salts that are liquid around room temperature, such as alkylammonium and phosphonium salts. Many of them are based on imidazolium and pyridinium cations.[20] Due to good electrical conductivity, heat stability and good corrosive resistance, ILs have been widely used as good solvents in many fields, such as electrochemistry, organic synthesis, catalysis and separation, *etc*.[21-23] ILs, doping in conducting polymers, have also been focused in recent years. For example, Dobbelin *et al.* have doped different ILs as permanent conductivity enhancers into PEDOT:PSS films, which showed improved electrical performance.[24]

In this work, twisted fiber ropes with enhanced conductivity were prepared by electrospinning of PEDOT:PSS-PVP doped with 1-ethyl-3-methylimidazolium acetate (EMIMAc, one kind of ionic liquid). For comparison, PVP doped with EMIMAc and PEDOT:PSS-PVP without EMIMAc doping were also electronspun. The PEDOT:PSS-PVP microropes doped with EMIMAc show enhanced electrical conductivity ($\sim 1.8 \times 10^{-4}$ S cm^{-1}), higher than those of other two kinds of microropes ($\sim 1 \times 10^{-5}$ S cm^{-1}). Meanwhile, the conductive microropes

exhibit outstanding mechanical behaviors. They can be stretched more than 90%, and then can be completely recovered, showing a linear reversible response. These interesting results indicate that the twisted PEDOT composite fibers may be used in some areas like stretchable sensors[25-27], elastic semiconductors[28] and flexible solar cells.[29-31]

2 Experimental

2.1 Electrospining apparatus

The experimental setup is illustrated in Figure 1. It consists of two parts: an electrospinning device for producing highly ordered nanofiber arrays (Figure 1a) and a motor device for twisting fiber array (Figure 1c). During electrospinning, the polymer nanofibers were well-aligned on the frame, and then the fiber array was taken down from the collector. Finally, the resulting fibers were twisted into a microrope by the motor device.
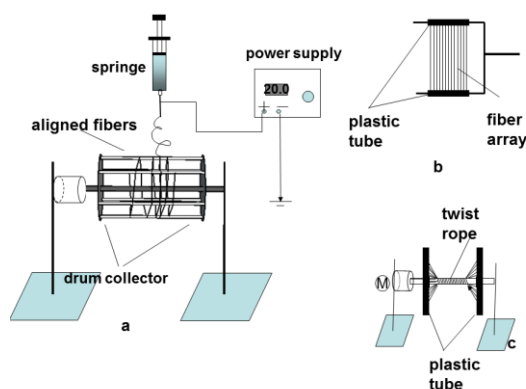
Fig. 1 Schematic illustration of the modified electrospinning setup; (a) aligned fibers were collected on the frame; (b) the fiber array was taken down from the frame collector; (c) the aligned fibers were twisted into a microrope.

2.2 Fabrication of PEDOT filaments by electrospinning

The precursor solution for electrospinning was prepared by dissolving 1.5 g of PVP (molecular weight: 16,000-20,000) into 3.0 g of PEDOT:PSS (2.8 wt% dispersion in H_2O, Sigma-Aldrich) and 5.5 g of absolute ethyl alcohol. Subsequently, 0.2 g EMIMAc was added into the solution. Stirred for 1 h at 60 °C, the solution became homogeneous. In this case, the dopant concentration was 1.96 wt%. For comparison, solutions with other concentrations (3.85, 5.66 and 7.41 wt%) were also prepared.

The composite solution was loaded into a plastic syringe for electrospinning. A high voltage of 15.0 kV was then supplied by a high voltage power supply (DW-P303-1ACFO, Tianjin Dongwen). The distance between the needle and collector was 8 cm. During electrospinning, the composite solution was fed at a steady flow rate of 0.25 ml h^{-1} by a digitally controlled syringe pump (LSP02-1B, Longer Pump). The humidity was controlled lower than 50%. After electrospinning about 10 min, highly ordered fiber array deposited on a pair of plastic tubes was taken down from the drum collector (Figure 1b) and transferred to the rotating device. As shown in Figure 1c, one tube was rotated with the motor and the other was fixed to the iron support. Subsequently, after 10 circles rotation, a twisted rope could be obtained.

2.3 Characterization

The electrospun fibers and twisted ropes were characterized by an optical microscope (Olympus BX51), a scanning electron microscope (SEM, DB235 FEI), and a Raman spectrometer (mps 3000, Laser Quantum). Electrical conductivities of the samples without stretching and in the tensile state were measured by a Keithley 6485 high resistance meter system at room temperature. A home-made device was used to stretch the samples.

3 Results and Discussion

3.1 Influence of ion liquid on fiber morphology

The electrospun polymer fibers have a wide range of diameter, ranging from hundreds of nanometers to tens of microns. The average fiber diameter (7.5 μm, 11.2 μm, 19.6 μm and 33 μm) increases gradually with the increase of IL doping (corresponding to 0, 1.96, 3.85 and 5.66 wt%, respectively), as shown in Figures 2 and 3.
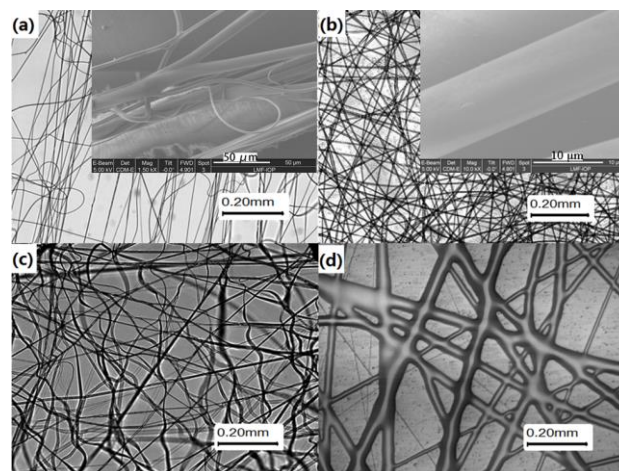
Fig. 2 Optical images of the PEDOT composite filaments via electrospinning with different EMMIAc concentrations: (a) 0; (b) 1.96; (c) 3.85; (d) 5.66 wt%.
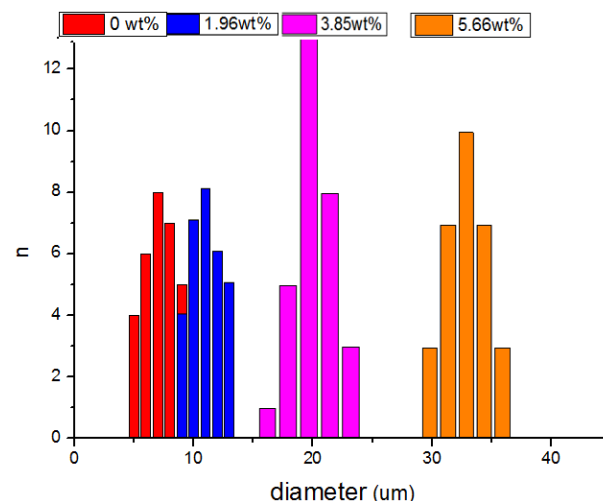
Fig. 3 Diameter analysis of the fibers with increasing doping level

In addition, the doping level of EMIMAc also influences the fiber surface morphology. The PEDOT composite fibers doped with EMIMAc (Figure 2b-d) are different from those undoped (Figure 2a). The fibers containing EMIMAc become more and more ropy and easier to absorb water with the increase of EMIMAc doping. When the addition of EMIMAc dopant increases over 7.41 wt%, the resulting filaments are difficult to dry timely because of low volatility of EMIMAc. 1.96 wt% of EMIMAc is suitable to produce good PEDOT fibers (In the following context, the results are mainly obtained from the samples with 1.96 wt% doping level). As the SEM images showed, the PEDOT/PSS-PVP fibers doped with ionic liquid EMIMAc have smooth surface.

3.2 Raman spectra

The diameter of twisted rope is about 180 μm (Figure 4). The structures of the resulting twisted filaments with and without EMIMAc doping were verified by Raman spectra, as shown in Figure 5. Comparing curve *b* and curve *c*, we can see the characteristic peaks of EMIMAc (e.g., 600, 1025 and 1336 cm^{-1}) appear in the spectrum of PEDOT/PSS-PVP doped with EMIMAc, indicating that the IL has been doped into the fibers indeed.

Fig. 4 Optical image and enlarged SEM image of a twisted PEDOT/PSS-PVP rope.

Fig. 5 Raman spectra of the fibers: (a) PEDOT/PSS-PVP; (b) PEDOT/PSS-PVP doped with EMIMAc; (c) pure ionic liquid of EMIMAc.

3.3 Electrical performance of the microrope devices

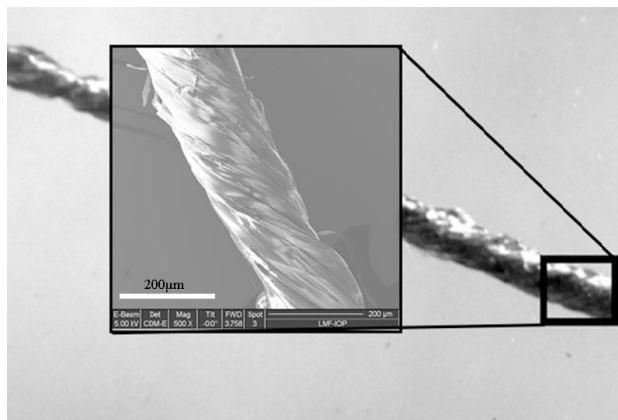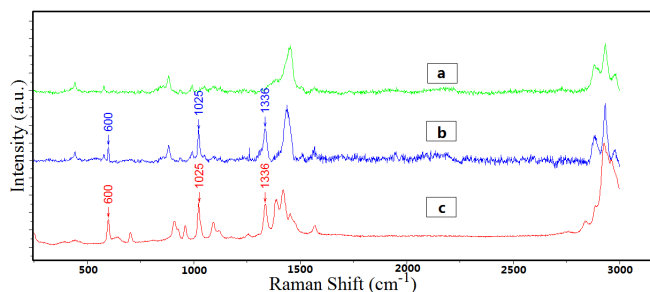Both the conductivities without stretching and in the tensile state were measured by a Keithley 6485 high resistance meter system and a home-made stretching device (Figure 6) at room temperature. This device could measure how long the fibers were stretched, and simultaneously, the electrical current through fibers was also measured under a fixed bias voltage.

Conductivity without stretching: As we know, PEDOT:PSS is made up of cationic PEDOT chain and anionic PSS chain. When the electron immigration or emigration from conjugate π bond chains of PEDOT, the radical ions and double ions produced make the polymer chain conductive.[32] In this study, the conductivity of PEDOT:PSS-PVP microropes with and
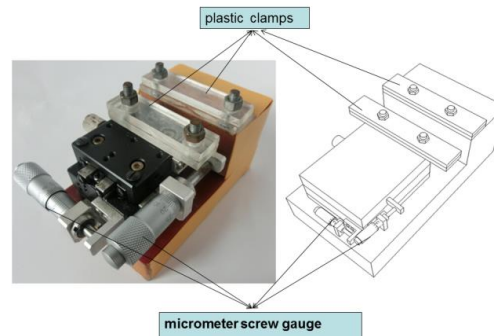

Fig. 6 Schematic illustration of the home-made device for stretching fibers
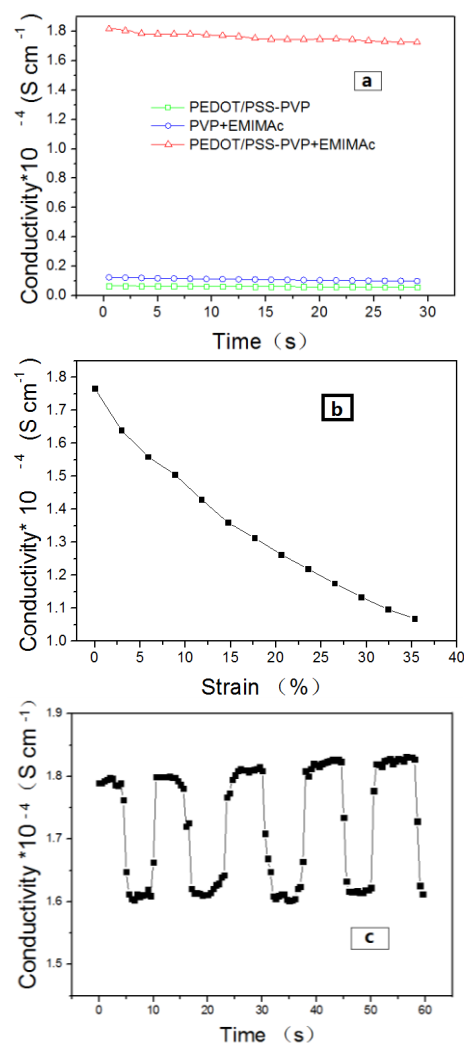
Fig. 7 (a) Electrical conductivity of the resulting fibers; (b) Conductivity change of the twisted PEDOT/PSS-PVP filaments doped with EMIMAc under continuous stretching; (c) Conductivity variety of PEDOT/PSS-PVP filaments doped with EMIMAc with a 5% repeated tensile-resilience.

without IL doping EMIMAc were measured. For comparison, the conductivity of the PVP fibers doped with EMIMAc was also tested, as showed in Figure 7a. We can see that the PEDOT:PSS-PVP ropes doped with EMIMAc show remarkably higher conductivity at room temperature, 1.8×10^{-4} S cm^{-1}, this value is one magnitude higher than those of undoped PEDOT:PSS-PVP sample and PVP rope with IL doping. Since the addition of EMIMAc into PVP (physical interaction) cannot enhance its conductivity to the magnitude of 10^{-4} S cm^{-1}, the increase in conductivity for PEDOT:PSS-PVP sample may be attributed to secondary doping effect (chemical interaction) of the ionic liquid EMIMAc, which severs as dopant like ordinary proton acid and increases doping level of PEDOT fibers.[33]

Conductivity in the tensile state: Another interesting advantage of the conductive PEDOT composite microrope is its excellent flexibility and stretchability. Figure 7b reveals the conductivity response of this sample to a continuous strain ranging from 0 up to 35%. During this stretching process, the conductivity only gradually decreases from 1.8×10^{-4} S cm^{-1} to 1.05×10^{-4} S cm^{-1}. Here, it should be noted that the strain (35%) in this work is one magnitude larger than that in previous reports. For example, a linear elastic resistance response to strain up to only 4% was reported for curled PEDOT composite fibers[16]. More importantly, the conductivity response to outer force has good circle loop with tensile-resilience. Figure 7c shows the conductivity response of the fibers to repeating strains. At the very beginning the fibers has stable conductivity (1.8×10^{-4} S cm^{-1}), as stretched uniform out to 2 mm (about 5% strain comparing with the original length) in 1 second, the conductivity declines to a low level ($\sim 1.6 \times 10^{-4}$ S cm^{-1}). Keep the 2 mm stretching for 6 s, then release. As the fibers restore, the conductivity recovers to the original level. Repeat this progress for several times, we can see the stretched and released conductivity could keep at a steady level. This valuable result suggests that the stretchable PEDOT:PSS-PVP microrope can be used as tensile sensor.
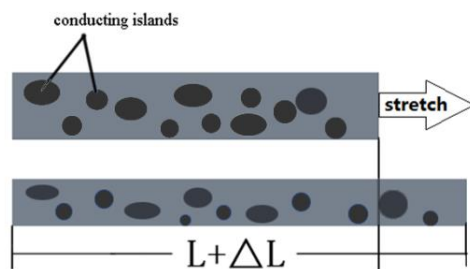
Fig. 8 Schematic illustration of a possible conduction model for the conductive composite fiber in the tensile state

In order to explain the conductivity response as shown in Figure 7b-c, a possible conduction model has been proposed. As we know, in the PEDOT:PSS-PVP composite fibers, PEDOT:PSS is the conductive component, which disperses in the insulative PVP matrix, just like many microscale "conducting islands"[34] embedded, as indicated in Figure 8. During stretching process, the composite fiber becomes longer and thinner, thus the distance between "conducting islands" increases gradually. Namely, the conduction (hopping and/or tunneling) distance from one conducting island to other islands

increases, resulting in the decrease of the fiber's conductivity. If this stretching process is not destructive for the composite fiber, the fiber's length as well as its conductivity can come back to the original values after releasing the strain.

3.4 Stretchability

The conductivity of the PEDOT:PSS-PVP microrope has an excellent linearity with strain, which also illustrates that the resulting microropes have good elasticity. But unlike metal, they are recoverable when outer force withdraws.

Table 1 Tensile elongation of PEDOT:PSS-PVP microropes doped with IL

IL dopping level (wt%)	Original length (cm)	Specific elongation (cm)	Resilience rate (%)
0	1.70	0.300	17.6
1.96	1.70	0.597	35.1
3.85	1.20	>1.1	>91.7

As shown in Table 1, the doped fibers can reach more than 90% resilience rate when the IL dopping level is 3.85 wt%. For comparison, the undoped sample can reach only 17.6% resilience rate, in fact, this value is already much larger than previously reported curled fibers[16]. The high stretchability of the PEDOT:PSS-PVP microrope could be ascribed to its twisted structure. However, the addition of EMIMAc enhances its stretchability significantly, which can be explained like this: besides doping function, the added EMIMAc also acts as a lubricating agent, decreases the friction drag among fibers. In addition, EMIMAc may decrease some fiber's defects, such as microvoids and microfractures.

Conclusions

We have employed an effective method to fabricate poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate)-polyvinyl pyrrolidone (PEDOT:PSS-PVP) nanofiber arrays and twisted microropes doped with ionic liquid (IL). It is noteworthy that the twisted rope exhibits higher electrical conductivity ($\sim 1.8 \times 10^{-4}$ S cm^{-1}) after IL doping (2 wt%) than those without IL doping ($\sim 0.8 \times 10^{-5}$ S cm^{-1}), and its conductivity is linear correlation with strain up as far as to 35% and shows repeatable cycle loop of tensile-resilience. The extensible rate could reach to more than 90%, much higher than that of ropes without IL doping (17%). The both excellent electrical and tensile properties can afford a possibility that the resulting PEDOT composite fibers could be used as tensile sensor, elastic semiconductors, and flexible solar cells.

Acknowledgements

Notes and references

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