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Core–sheath functional polymer nanofibers prepared by co-electrospinning

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Abstract

Core–sheath polymer nanofibers with optoelectronic materials as the sheath and easily spinnable polymer as the core were prepared by co-electrospinning. Three prototypical systems of polystyrene/poly(*p*-phenylene vinylene) (PS/PPV), poly(vinyl alcohol)/poly(*p*-phenylene vinylene) (PVA/PPV) and polystyrene/tris(8-quinolinolato) aluminum (PS/Alq_3) were investigated. The fluorescence microscopy images showed that the resulting nanofibers with uniform morphologies exhibited outstanding emission properties. The core–sheath structures of these nanofibers were observed by TEM investigation. The photoluminescence spectra indicated that the fluorescent properties of these functional core–sheath nanofibers could be influenced by the interaction between core and sheath materials.

Keywords: Core–sheath; Polymer fibers; Fluorescent; Co-electrospinning

1. Introduction

Production and control of one-dimensional (1D) nanostructures with various morphologies and functionalities play an important role in constructing nano-/microscale devices, such as nano-/micro-optoelectronic devices. Notably, electrospinning (a drawing process based on electrostatic force) was developed to fabricate 1D nanomaterials in recent decades [1–3]. The high surface area-to-volume ratio of the electrospun fibers makes them suitable for many applications such as filtration [4], sensing [5], catalysis [6], tissue engineering [7], and protective clothing [8]. In addition, many electrospun nanofibers with interesting morphologies, such as the bead-on-string [9] and helical [10] structures, have potential applications in many areas including advanced photonic components, structural or inductive components in micro-electromechanical systems devices, and drug delivery systems. Currently, more than 50 different polymers have been electrospun into nanofibers. However, many functional materials are difficult to be directly electrospun as limited by their molecular weights and solubilities.

Recently, the immobilization of functional materials on the surface of electrospun fibers by coating to fabricate core–sheath functional fibers has been demonstrated [11,12]. This fabrication process often needs two or three steps and has difficulty creating

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core–sheath nanofibers with long length due to interconnections between fibers formed during the coating step. Another approach to fabricate the functional electrospun fibers is blend-electrospinning, which is limited to materials that can form a homogeneous solution in a solvent or solvents mixture. Besides these available approaches, newly emerged co-electrospinning [13–16] would provide a simple and versatile means to produce functional composite nanofibers. With co-electrospinning, two components can be coaxially and simultaneously electrospun through different feeding capillary channels to generate composite nanofibers in the form of core–sheath structure. This approach was often used for those core materials with functional properties that were not able to be electrospun directly, such as dispersion of drugs. In these core–sheath fibers, the sheath polymers served as a template for the core materials leading to compartment-type structures. However, many functional materials are expected to be rich on the surface to enhance material property profiles for applications including photonics. In this paper, we report that the core polymer served as the template and conjugated polymer poly(*p*-phenylene vinylene) PPV [17] and organic dye molecule tris(8-quinolinolato) aluminum (Alq_3) [18] were coated on the surface of the core fiber by co-electrospinning. The major advantage of this core–sheath nanostructure is the potential to combine the functionalities of functional materials and the morphologies of electrospun polymer fibers.

2. Experimental

2.1. Materials

p-Xylylene dichloride (98%) and tetrahydrothiophene (98%), purchased from Aldrich, were used to prepare the PPV precursor. PS ($M_w \approx 190\,000$) and PVA ($M_w \approx 78\,000$) were purchased from Aldrich and used without further purification. Alq_3 was supplied by Tokyo Kasei Kogyo Co., Ltd. (Japan).

2.2. Preparation of core–sheath functional polymer nanofibers

The basic experimental setup for co-electrospinning process is similar to the setups demonstrated by other groups [15–18]. The spinneret consisted of a syringe-like apparatus with an inner stainless steel needle coaxially placed inside an outer one. The inner needle had an inner diameter (ID) of 0.27 mm and an outer diameter (OD) of 0.6 mm. The ID of the outer needle was 0.9 mm. The inner needle protruded from the outer needle by about 0.3 mm. A high voltage direct current (DC) power supply (model 74900-05, Cole Parmer Instrument Company) was connected on the outer stainless steel needle to electrically charge the polymer solution. Two syringe pumps (type YBWZ-12) were used to deliver core and sheath solutions. The electrospun nanofibers were collected on a grounded aluminum foil or two parallel aluminum strips.

The core–sheath matrix/PPV fibers were electrospun from PPV precursor solution and matrix polymer solutions. The precursor as sheath polymer was synthesized following the standard polyelectrolyte route [19] and this route has been used widely for the synthesis of high molecular weight PPV. The precursor polymer was kept in ethanol at a concentration of approximately 1 wt% after dialyzed against ethanol for several days. PPV precursor nanofibers were electrospun from this solution. To fabricate PS/PPV fibers, DMF solution of 25 wt% PS as core solution was prepared. During the co-electrospinning process, the flow rates of the outer and the inner solutions were 0.5 and 1 ml/h, respectively. The applied voltage was 12 kV and the distance between the needle tip and the collector was 23 cm. For the PVA/PPV nanofibers, 7 wt% PVA in water as core solution was prepared. The flow rates of the outer and the inner solutions were both fixed at 1 ml/h. The potential was 10 kV and the distance between the needle tip and the collector was 17 cm. After the process of electrospinning, the electrospun fibers were all heated at 180 °C for 1 h in a vacuum oven for conversion of the precursor to PPV. For the PS/Alq_3 fibers, DMF solution of 1.5 wt% Alq_3 as the sheath and THF solution of 20 wt% PS as the core were prepared. The flow rates of the outer and the inner solutions were 0.5 and 1 ml/h, respectively. The potential was 12 kV and the distance between the needle tip and the collector was 21 cm.

2.3. Characterization of electrospun nanofibers

Fluorescent images of the fiber samples were obtained using a fluorescence microscope (Olympus BX51). The core–sheath structures of these fibers were observed using TEM (Hitachi H-8100) operated at 100 kV. The PL measurements were performed using a Shimadzu RF-5301 PC spectrofluorimeter.

3. Results and discussion

3.1. Core–sheath structure of electrospun fibers

To investigate the core–sheath structure of these functional nanofibers, TEM observation was conducted. Although the two solvents (core DMF and sheath ethanol) are miscible, the two polymers (core PS and sheath PPV precursor) are immiscible. Hence, sharp boundaries of the core–sheath structure can be seen in PS/PPV fibers (Fig. 1a). However, the boundaries between core and sheath of the PVA/PPV are unobvious (Fig. 1b). This observation suggests that the PPV precursor fluid may be mixed with the PVA fluid to some extent during the electrospinning process due to PVA and PPV precursor can form a homogeneous solution in aqueous solvent. We also demonstrated the polymer/small molecule system of PS/Alq$_3$ can be co-electrospun into core–sheath structure. PS is a common spinnable polymer and often used as matrixes for the fabrication of the core–sheath micro-spheres and fibers [20,21]. In addition, PS can be blended well with Alq$_3$ in solution. The TEM image in Fig. 1c shows that the Alq$_3$ and PS were electrospun into core–sheath structure with unobvious boundaries in some sections and uneven sheath thick along the fiber. During the co-electrospinning, the sheath fluid composed of Alq$_3$ could filter into the core fluid due to the well diffusibility of small molecule. The entraining could arise from this slight mixing of Alq$_3$ and PS, and then the core–sheath structure is formed without the splash of the Alq$_3$ fluid under the electric field.

3.2. Morphology and diameter distribution of electrospun fibers

The morphologies and functionalities of the core–sheath co-electrospun fibers can be controlled by choosing different core and sheath materials. Fig. 2 presents the fluorescence microscopy images and the diameter distribution of core–sheath PS/PPV, PVA/PPV and PS/Alq$_3$ fibers. The diameter distribution of every kind of electrospun fibers was statistic from 200 fibers. As shown in Fig. 2a and c, the morphologies of the PS/PPV and PS/Alq$_3$ fibers are consistent with the morphology of electrospinning PS in DMF and electrospinning PS in THF [22], respectively. However, the core–sheath PVA/PPV fibers show a helical morphology, which is different from the electrospun PVA fibers (Fig. 2b). The helical PVA/PPV fibers formation could be attributed to the large amount of PPV

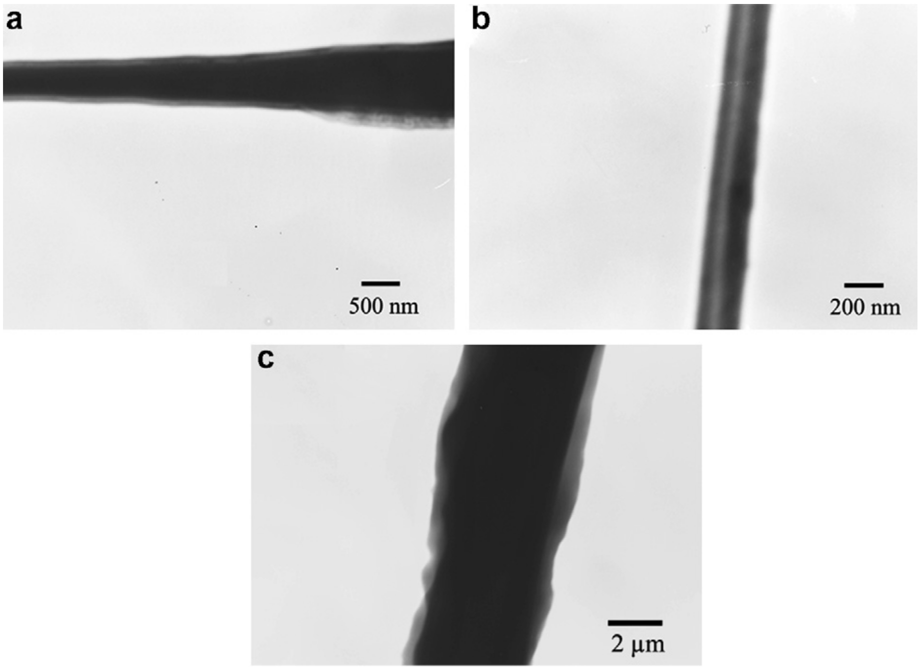

Fig. 1. TEM images of core–sheath: (a) PS/PPV, (b) PVA/PPV, and (c) PS/Alq$_3$ fibers.

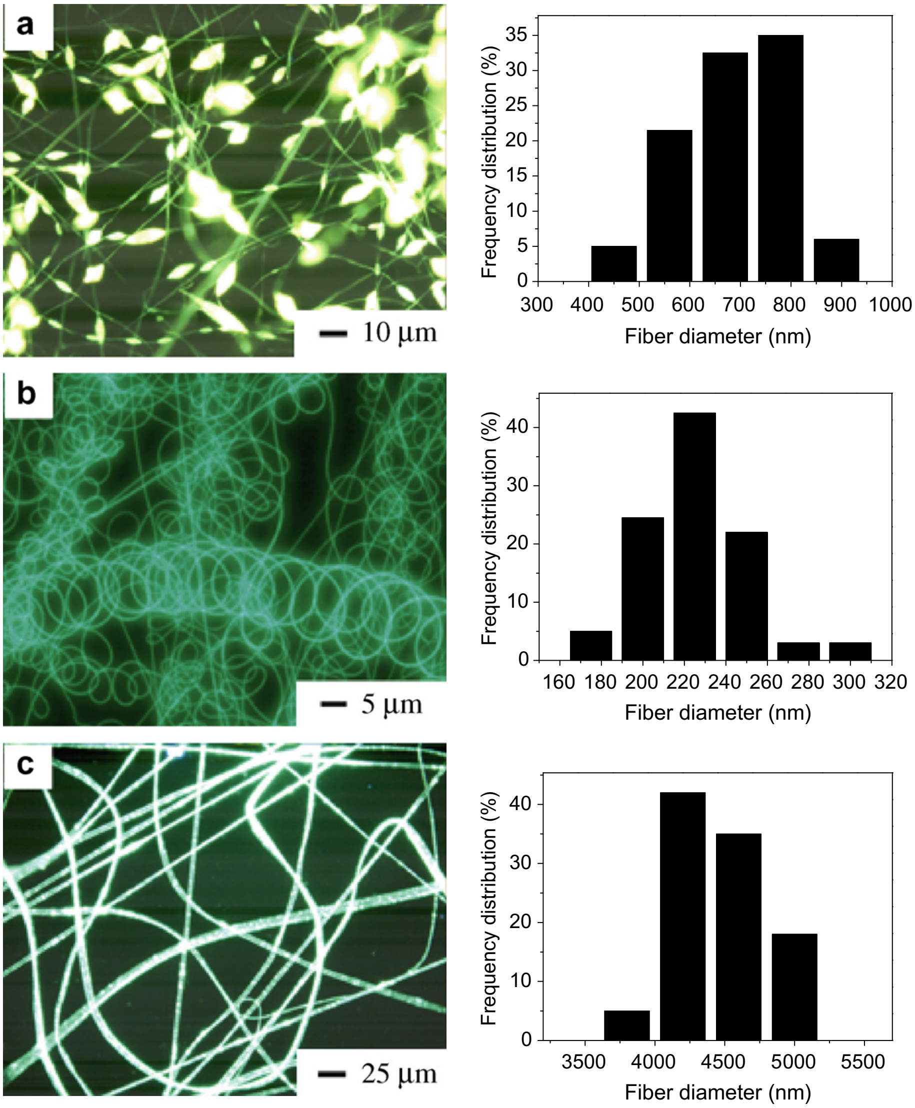

Fig. 2. Fluorescence microscopy images and diameter distribution of core–sheath: (a) PS/PPV, (b) PVA/PPV, and (c) PS/Alq_3 fibers.

and the mixing of PPV precursor and PVA in core–sheath PVA/PPV fibers. As shown in the TEM image of core–sheath PVA/PPV fibers (Fig. 1b), the PPV sheath is much thicker than the PVA core, which indicates that the electrospinning core–sheath PVA/PPV jets are mainly composed of PPV precursor. The PPV precursor is a cationic polyelectrolyte, and the charged PPV precursor jets undergo much higher electrostatic repulsive forces than common spinnable polymers during electrospinning [23,24]. In addition, the mixing of PPV precursor and PVA increased the viscosity of the electrospinning jets. The high conductivity and viscosity of the charged jets may increase the degree of bending instability [25] in electrospinning. Thus, the highly charged viscous jets tightly looped and were preserved in the shape of solid fibers. It can also be seen from Fig. 2 that the average diameters of these core–sheath fibers are similar with pure PS and PVA electrospun fibers, respectively. In short, the morphology and the average diameter of these electrospun core–sheath functional fibers are mainly influenced by core polymer.

The core–sheath PVA/PPV nanofibers can also be collected with uniaxially aligned form by the parallel electrodes [26], however the PPV nanofibers electrospun from PPV precursor were not able to be collected as well-aligned structures (Fig. 3a

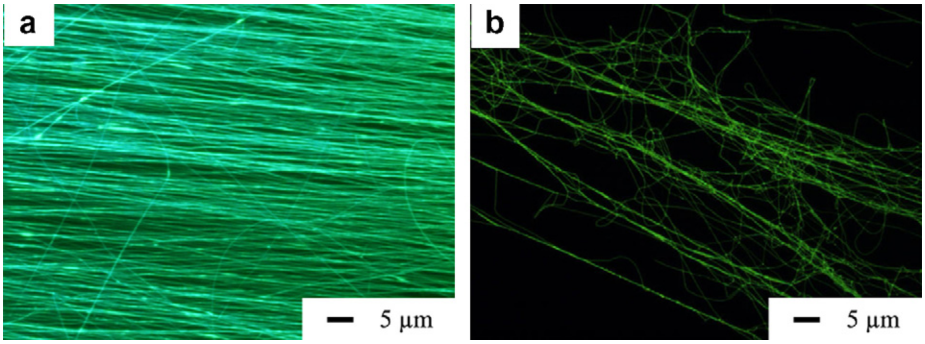

Fig. 3. Fluorescence microscopy images of (a) core–sheath PVA/PPV and (b) pure PPV fibers both collected by the parallel electrodes.

and b). This phenomenon was also observed when collecting PPV precursor fibers on rotating collectors [27,7]. The PPV precursor, as a polyelectrolyte, contains a charged atom in each repeating unit. Hence, the PPV precursor charged jets may undergo a more complex instability [25] during the electrospinning, and then the precursor fibers deposited on these collectors were not well-aligned. The core–sheath PVA/PPV precursor charged jets could be more stable than pure PPV precursor due to the introducing of the core PVA. Therefore, the controlled deposition of the PVA/PPV precursor nanofibers was achieved.

3.3. Fluorescence spectra

The PL emission spectra were performed to study the fluorescent properties of the core–sheath fibers. As shown in Fig. 4, the core–sheath PS/PPV and PS/Alq$_3$ fibers emit fluorescence in yellow–green range and green, as the pure PPV fibers and bulk Alq$_3$, respectively. However, the core–sheath PVA/PPV fibers exhibit blue-shifted emission and redistribution of intensity compared with PPV and core–sheath PS/PPV fibers. This observation is similar to the PPV/PVA blend film relative to PPV film [28]. The differences in PL spectra may be attributed to the reaction on the interface of the core and sheath since it is known that the precursor polymer can react with PVA's OH groups to form ether groups on the linkages between the phenyl rings of the polymer backbone, which will shorten the conjugated chain length of PPV. The PL spectra of core–sheath PS/PPV fibers is similar to that of PPV fibers, which may be resulted from the immiscible property of the two polymers (core PS and sheath PPV precursor).

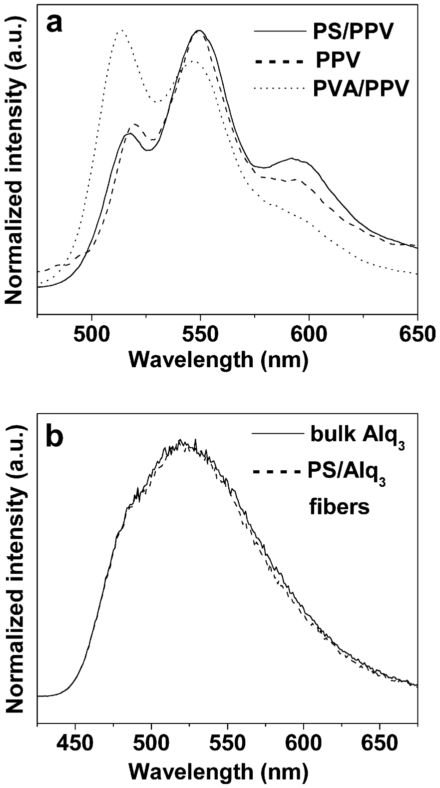

Fig. 4. (a) PL spectra obtained from core–sheath PS/PPV, pure PPV, and core–sheath PVA/PPV fibers. (b) PL spectra obtained from bulk Alq$_3$ and core–sheath PS/Alq$_3$ fibers.

4. Conclusion

In summary, we have patterned optoelectronic materials on polymer nanofibers to form core–sheath structures directly by co-electrospinning. We found that the resulting nanofibers exhibited the advantaged characteristics of both core and sheath materials such as excellent functional properties of the sheath, and available morphologies of core materials. For example, the core–sheath PS/PPV fibers with outstanding emission properties exhibited a bead-on-string morphology. The micrometer size and spherical shape of these PS/PPV beads suggest that these structures will have intriguing photonic properties, which is similar to those found in dielectric microsphere [29] and suspended micrometer liquid droplets [30]. These nanofibers are potentially interesting for various applications such as micro- and nanodevices and systems. This investigation provides an easy method for functionalizing polymer nanofibers on surface.

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