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click for updatesFlexible electroluminescent fiber fabricated from
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A fiber-shaped polymer light-emitting electrochemical cell (PLEC) was developed by sandwiching an electroluminescent polymer layer between two aligned carbon nanotube (CNT) sheet electrodes. Similar to a conventional planar PLEC, the electroluminescent polymer layer and two carbon nanotube electrodes are closely and stably contacted, so that the injected charges can be rapidly and efficiently transported. Due to their one-dimensional structure, the fiber-shaped PLEC demonstrates unique and promising advantages, e.g., the luminance is almost independent on the observation angle. In addition, the fiber-shaped PLEC is thin, lightweight and flexible, which bespeaks a promising future for various electronic textiles.

Introduction

Wearable electronics have emerged as a promising direction in electronic materials and devices and is proposed as a breakthrough technology in the near future.^{1–6} Among the many explored electronic products, light-emitting devices represent one of the mostly explored directions. Recently, increasing interests are attracted to develop electronic devices in a fiber shape to satisfy wearable applications because the fiber-shaped devices are lightweight and weavable when compared with their conventional planar counterparts. Although both fiber-shaped energy harvesting and storage devices have been extensively studied,^{7–11} it remains challenging to make fiber-shaped organic light-emitting diodes (OLEDs) and polymer light-emitting diodes (PLEDs), which are the two main families of light-emitting devices.^{12–14} When compared with the conventional planar structure, it is more difficult to

accurately control the thickness and evenness of the active layers for an effective absorption of multilayer active materials in a fiber-shaped OLED or PLED through a continuous layer-by-layer dip-coating process.

In contrast, polymer light-emitting electrochemical cells (PLECs), which do not require a layer-by-layer coating process, become promising in the development of fiber-shaped light-emitting devices because they may be made into an all-solid-state structure with easy operation during use.^{15–17} In addition, the electroluminescent polymer layer of the PLEC is sandwiched between two electrodes to form a light-emitting PIN junction *in situ* for the injections of both electrons and holes from the electrodes without the use of low work-function cathodes that are sensitive to air.^{18–25} Although fiber-shaped PLECs have been highly desired for many years, the continuous preparation of fiber-shaped PLEC on a large scale is still unavailable due to the difficulty in finding appropriate fiber electrode materials that are flexible, electrically conductive, optically transparent and thermally stable.

Aligned carbon nanotube (CNT) sheets have been recently demonstrated for their combination of remarkable mechanical, electronic, optical and thermal properties.^{7,8} Such CNT sheets are flexible and can be tightly wrapped onto a fiber substrate. They may even be closely attached onto soft and curved substrates derived from the aligned nanostructure on the contact surface. The aligned structure of CNTs also provides high electrical conductivities that are well maintained under bending or other deformations of the sheets. They are thin and transparent and can be effectively used as electrodes for various optoelectronic devices. The CNT has also been shown to display high stability, which is promising for stable electronic devices.

In this Communication, we have developed a fiber-shaped PLEC (or called “luminescent fiber”) by sandwiching an electroluminescent polymer layer between two aligned CNT sheet electrodes. Similar to a conventional planar PLEC,²⁶ the electroluminescent polymer layer and two CNT electrodes are closely and stably contacted, so that the injected charges can be rapidly and efficiently transported. Due to its one-dimensional structure,

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the “luminescent fiber” demonstrates unique and promising advantages, *e.g.*, the luminance is almost independent on the observation angle. In addition, the “luminescent fiber” is thin, lightweight and flexible, which bespeaks a promising future for various electronic textiles.

Experimental section

Fabrication of the “luminescent fiber”

The aligned CNT sheet was continuously and uniformly wrapped onto an insulating fiber. Polyfluorene copolymer (PF-B), ETT-15 and LiTf were dissolved in anhydrous, inhibitor-free tetrahydrofuran with weight ratios of 20/10/1 (PF-B concentration of 40 mg mL⁻¹).⁶ The yellow light emissive conjugated polymer (SuperYellow), ETT-15, PEO and LiTf were dissolved in tetrahydrofuran with weight ratios of 20/2/2/1 (SuperYellow concentration of 3.5 mg mL⁻¹).¹⁷ The above-mentioned mixture was uniformly dip-coated onto the conducting fiber substrate and dried in vacuum for 1 h. Finally, another aligned CNT sheet with a thickness of 18 nm was wrapped onto the outer surface of the electroluminescent polymer layer using the same method to produce a “luminescent fiber”. An aligned CNT sheet was wrapped onto the emissive polymer-coated fiber to produce the fiber-shaped PLEC with lengths of millimeters to centimeters. For the convenience of characterization, two electrodes of the fiber-shaped PLEC were connected with indium using an ultrasonic soldering mate (USM-V, Kuroda Techno).

Results and discussion

Fig. 1 schematically shows the fabrication process for the “luminescent fiber” starting from a fiber substrate. An aligned CNT sheet was first continuously and uniformly wrapped onto

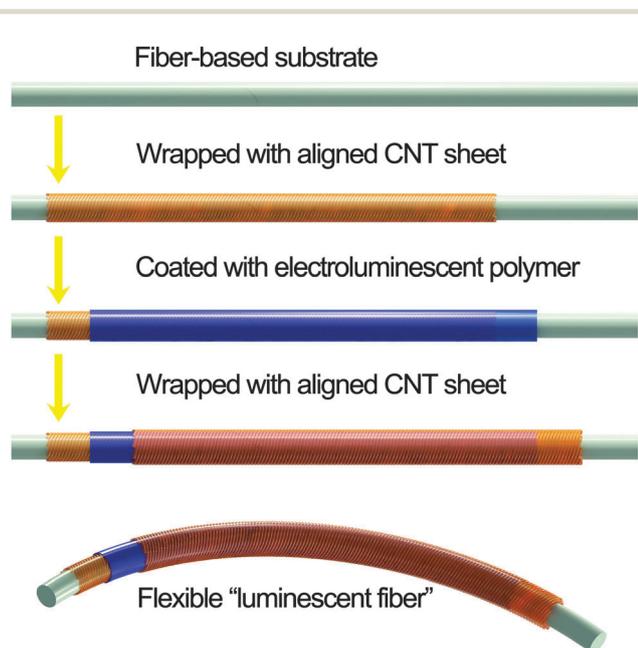


Fig. 1 Schematic illustration of the fabrication of a “luminescent fiber”.

an insulating fiber substrate to serve as the inner electrode (cathode), followed by dip-coating the electroluminescent polymer layer and then winding another aligned CNT sheet (anode) onto the outer surface of the electroluminescent polymer layer to produce the designed “luminescent fiber”. Due to the formation of light-emitting PIN junction *in situ*, the “luminescent fiber” does not require the electron and hole transfer layers.

Fig. 2a shows a typical scanning electron microscopy (SEM) image of an insulating fiber. The wrapping process of the aligned CNT sheet is schematically shown in Fig. S1 (ESI[†]), and the detailed synthesis of the spinnable CNT array is described in the ESI.[†]⁶ The thickness of the wrapped aligned CNT sheet can be controlled by varying the width of the aligned CNT sheet and the wrapping angle (α) and number. The wrapped CNTs remain highly aligned on the fiber (Fig. 2b).^{27,28} The fiber electrode with the aligned CNT sheet on the surface was flexible and no damage in the structure was observed by SEM. In addition, the resistance of the CNT sheet-modified fiber (with a diameter of 325 μm) showed an average electrical resistance of 1000 $\Omega\text{ cm}^{-1}$ that was varied below 10% after bending with a radius of the curvature of 9 mm for 500 cycles (Fig. S2, ESI[†]). The aligned CNT sheet was transparent with a transmittance over 87% at the wavelength above 550 nm for a CNT sheet with thickness of 18 nm (Fig. S3, ESI[†]).

The surface of the electroluminescent polymer layer was smooth without any evident aggregations (Fig. 2c). Similar to the CNT sheet cathode, the outer CNT remained aligned as the anode (Fig. 2d). Due to the high contact area between the aligned CNT sheet and electroluminescent polymer layer, the aligned CNT sheet can be closely attached to the insulating fiber substrate mainly by van der Waals forces. This advantage is particularly important for the high and stable performance of the “luminescent fiber”. The two electrodes were connected to external circuits for characterization (Fig. S4, ESI[†]).

The electrochemical reactions of the “luminescent fiber” occurred upon the application of a sufficient voltage: the light-emitting conjugated polymer becomes n-doped along the cathode side and p-doped along the anode side.^{18–20} The PIN junction formation allows the use of a high work function cathode and thicker electroluminescent polymer layers without impairing the device performance. In the “luminescent fiber”, the electrons and holes are injected into the electroluminescent polymer layer through the inner and outer aligned CNT sheet electrodes, respectively.

For the “luminescent fiber”, the electroluminescent polymer layer consists of a blend of a light-emitting polymer (PF-B), ethoxylated trimethylpropane triacrylate (ETT-15) and lithium trifluoromethanesulphonate (LiTf) (Fig. S5, ESI[†]).²⁹ PF-B was studied as a demonstration due to its high electroluminescent performance, ETT-15 was used as an ionically conductive component, and LiTf, which is a widely used salt in solid electrolyte, provided the ionic dopant for the doped polymer in the formation of the PIN junction.

The current density–luminance–driving voltage and current efficiency–luminance characteristic curves of a typical “luminescent fiber” are presented in Fig. 3a and b, respectively. Light emission occurred at ~ 8.8 V, and the highest brightness

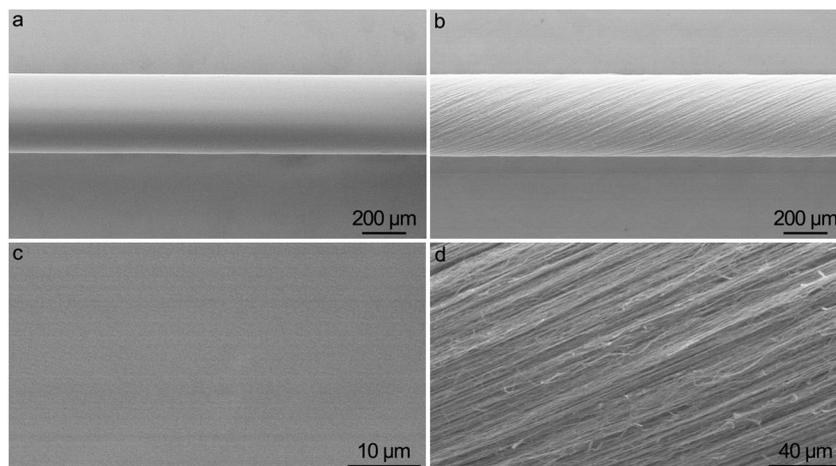


Fig. 2 Structural characterization. (a) An insulating fiber substrate. (b) Aligned CNT sheet wrapped on the fiber substrate. (c) Electroluminescent polymer layer coated on the aligned CNT sheet. (d) Aligned CNT sheet wrapped on the electroluminescent polymer layer.

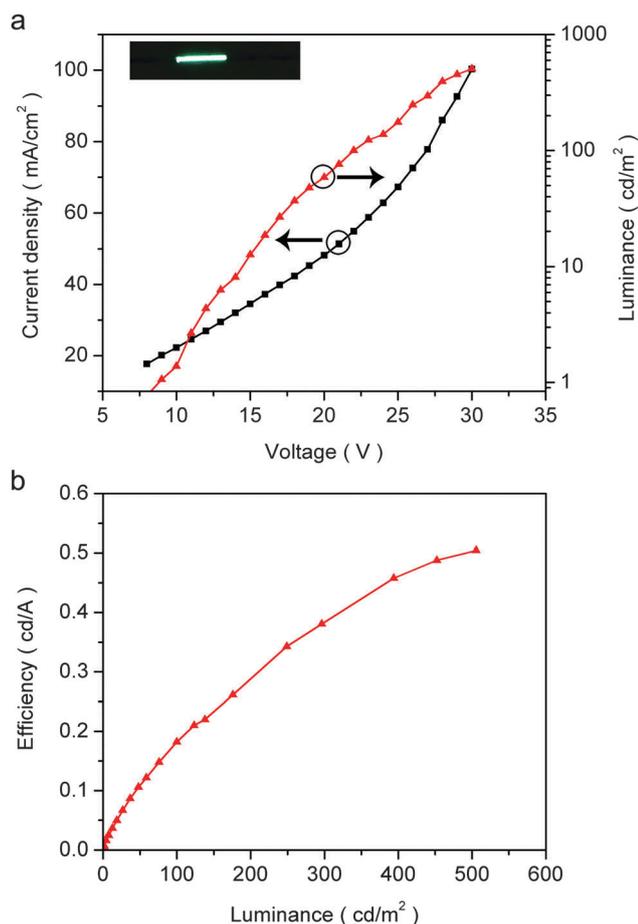


Fig. 3 (a) Current density–luminance–driving voltage characteristics of the “luminescent fiber”. Inset image shows a “luminescent fiber” with a length of nearly 2.6 cm lightened at 16 V. (b) Current efficiency–luminance characteristic of the “luminescent fiber”.

reached 505 cd m^{-2} . The current efficiency was increased with increasing brightness and reached 0.51 cd A^{-1} at the end. According to the CIE 1931 standard color-matching functions,

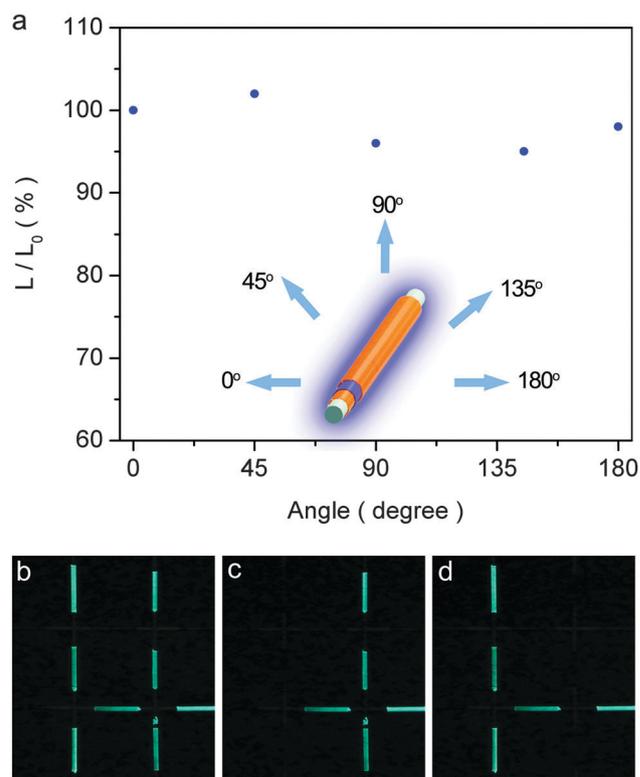


Fig. 4 (a) The dependence of luminance on the observation angle for a “luminescent fiber”. Here L_0 and L correspond to the luminance measured at 0 and at other observation angles, respectively. (b–d) Images of woven “luminescent fibers” being selectively lightened (with a diameter of $325 \mu\text{m}$ and length of $\sim 2.8 \text{ cm}$, biased at 16 V).

it is expressed as (0.22, 0.36) by the x, y chromaticity coordinates. The inserted image further shows a blue “luminescent fiber” with a diameter of $325 \mu\text{m}$ as expected, which exhibits a uniform emission across the entire light-emitting area.

The turn-on response of light emission from the PIN junction in the electroluminescent polymer layer was also investigated by

a pulse voltage operation (Fig. S6, ESI[†]), and the pre-charged PLEC demonstrated a rapid turn-on response. This “luminescent fiber” exhibited some unique and promising advantages. For instance, the luminance was almost independent on the observation angle (Fig. 4a) and the brightness had been varied below 6%. Fig. S7a and b (ESI[†]) compare the SEM images of the outer aligned CNT sheet before and after bending. Evidently, the aligned CNT sheet remained highly aligned and uniform without being peeled off from the fiber substrate. In addition, the brightness has been maintained at 91.2% even after bending with a radius of the curvature of 9 mm for 100 cycles (Fig. S8, ESI[†]).

It is notable that the blue light “luminescent fiber” was investigated as a demonstration and other colors can also be produced by changing the electroluminescent polymer layer. For example, a yellow light “luminescent fiber” can be achieved by replacement with a yellow light electroluminescent polymer layer. According to the CIE 1931 standard color-matching functions, it is demonstrated by the *x*, *y* chromaticity coordinates of (0.46, 0.52) (Fig. S9, ESI[†]). Due to its flexibility and weavability, the “luminescent fiber” can be further woven into electronic clothes that can exhibit different patterns (Fig. 4b–d).

Importantly, there is a large scope to further enhance the performance of the “luminescent fiber” compared with a conventional planar PLEC. A lot of efforts are underway to increase the brightness and decrease the operating voltage by improving the electronic properties of the aligned CNT sheets, e.g., the electrical conductivities may be largely enhanced by lengthening the CNTs used during the synthesis.^{30,31}

Conclusions

In summary, a novel “luminescent fiber” has been developed by designing a coaxial sandwiched structure based on two aligned CNT sheet electrodes. The fiber shape offers unique and promising advantages. For instance, the brightness of the symmetrical fiber device is almost the same in all directions, which proves necessary for micro-electronic applications. It is thin, lightweight and weavable, and represents a new family of light-emitting devices for wearable electronic textiles.

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