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Dual-function optoelectronic polymer device for photoelectric conversion and electroluminescence†

Zhitao Zhang, Lie Wang, Yiming Li, Xueyi Li, Guozhen Guan, Ye Zhang and Huisheng Peng*

A novel polymer-based optoelectronic device is created to independently realize either photoelectric conversion or light emission. It is produced by coating photoactive materials on one side of an aligned carbon nanotube sheet electrode and polymer light-emitting materials on the other through an all-solution process. The power conversion efficiency exceeds 2% and the brightness reaches 1040 cd m⁻² for photoelectric conversion and light emission, respectively. This study indicates a promising potential for the all-solution-based process for a wide variety of applications, including microelectronics, and smart and multi-function devices.

Multi-function devices have been recognized as a mainstream direction in the development of next-generation electronics and may be extensively used in biomedical, military and aerospace fields.^{1–6} They can remarkably reduce the number of electronic devices whilst perceiving required functions to commendably meet the requirements of many new and emerging fields, for example, portable electronic devices. Currently, much interest centers around development of polymer-based electronic devices,^{7–13} e.g., polymer-based energy storage devices, polymer solar cells, polymer light-emitting diodes and polymer light-emitting electrochemical cells (PLECs), owing to their many advantages, including the diversity of polymer materials and the possibilities of an all-solution-based process and large-scale production. More importantly, they can be made into flexible and thin films, which satisfy the widely explored portable electronic devices.^{14–16} A variety of polymer-based electronic devices have been stacked to realize multiple functions but with a tedious fabrication process, a complex structure and a low performance.^{1,3} The situation is far away from the truly integrated single device that has been desired for many years to display two or more functions in a concise and elegant design.

In this study, we have developed a novel polymer-based optoelectronic device that can independently realize either

photoelectric conversion (PC) or light emission (LE). It is produced by coating photoactive materials on one side of an aligned carbon nanotube (CNT) sheet electrode and polymer light-emitting materials on the other through an all-solution process. The power conversion efficiency exceeds 2% and the brightness reaches 1040 cd m⁻² for the PC and LE properties, respectively.

The structure of the dual-function device is schematically shown in Fig. 1. For the PC part, the ZnO nanoparticles have been used as the electron-transporting layer.¹² The crystalline nanoparticles with diameters of appropriately 6 nm (Fig. S1, ESI†) were spin-coated onto the indium tin oxide (ITO) substrate to produce a uniform and compact layer (Fig. 2a). The thickness of the ZnO nanoparticle layer was increased and controlled by repeating the coating process. The selective nature of the ZnO nanoparticle layer is necessary and important to achieve a high performance in the PC part.¹² The photoactive layer of poly(3-hexylthiophene):phenyl-C₆₁-butyric acid methyl ester (P3HT:PCBM) has then been spin-coated onto the ZnO layer that was also uniform (Fig. 2b).¹⁷ Aligned carbon nanotube (CNT) sheet was further laid onto the P3HT/PCBM surface to serve as a hole-transporting layer

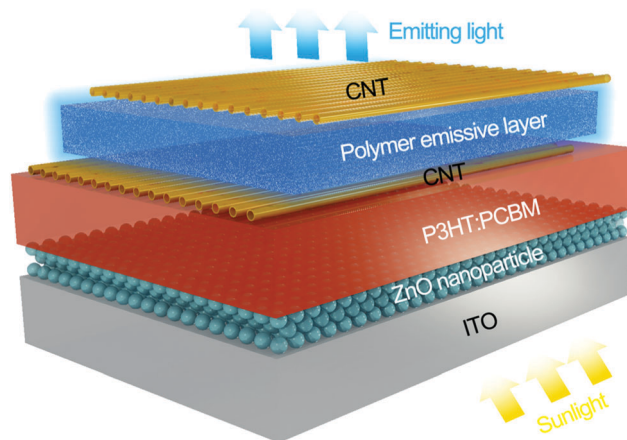


Fig. 1 Schematic of the structure of the dual-function optoelectronic device.

State Key Laboratory of Molecular Engineering of Polymers,
Department of Macromolecular Science, and Laboratory of Advanced Materials,
Fudan University, Shanghai 200438, China. E-mail: penghs@fudan.edu.cn

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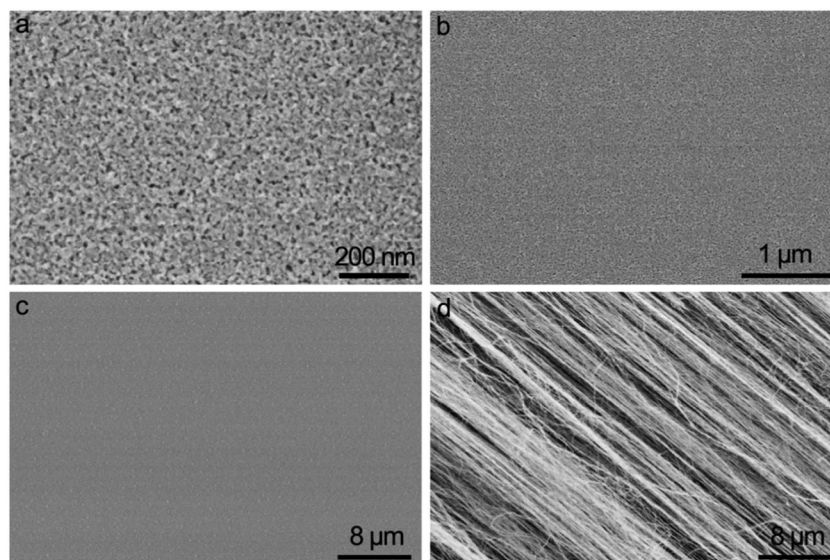


Fig. 2 SEM images of the dual-function optoelectronic device. (a) ZnO nanoparticle layer. (b) P3HT:PCBM layer. (c) Emissive polymer layer. (d) Aligned CNT sheet.

and electrode to obtain the PC part. The aligned CNT sheet was prepared from a spinnable CNT array and described in the ESI†^{18,19} It was flexible and could be easily bent or twisted into various shapes without obvious damage to the structure. In addition, it was also transparent and electrically conducting.^{18,19} Therefore, the CNT sheet may serve as a high performance, flexible electrode in the device.

Note that the PC part was fabricated without using the hole-transporting layer, *e.g.*, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), as the existence of water and acid in the PEDOT:PSS solution was harmful to the polymer active layer.²⁰ Moreover, the fabrication of the PC part was remarkably simplified to benefit large-scale applications. The PC part had been fabricated with an inverted structure. The inverted structure was beneficial for the vertical phase separation in the photoactive layer and avoided the use of low work function electrodes that were sensitive to air and needed a complex preparation with high cost.^{21,22} As a result, the PC part shared the high work function CNT electrode with the LE part. Moreover, the CNT electrode has also been used as an air-stable layer for the device.

Polymer light-emitting electrochemical cells (PLECs) are explored as a new family of effective electroluminescent devices.^{23,24} The PLEC accepted as the simplest light-emitting device is usually composed of an organic semiconductor sandwiched between two electrodes, which inspired us to design the LE part in this study. First, the emissive polymer layer was spin-coated at the top of the aligned CNT sheet (Fig. 2c). Herein, the emissive polymer layer used was composed of an emissive conjugated polymer (PF-B) (Fig. S2, ESI†), lithium trifluoromethanesulphonate (LiTf) and ethoxylated trimethylpropane triacrylate (ETT-15).^{9,15} ETT-15 and LiTf serve as an ionically conductive component and an ionic dopant, respectively, for the formation of a light-emitting PIN junction. Finally, another aligned CNT sheet electrode (Fig. 2d)

was laid onto the emissive polymer layer to complete the LE part. The electroluminescent polymer layer of the LE part can form a light-emitting PIN junction *in situ*.¹³ The PIN junction can be operated at rough surfaces, which is beneficial for many practical applications with low cost and high efficiency.

The PC and LE functions can be independently operated by connecting the middle CNT sheet electrode with the electrodes in the two other parts. When the middle CNT sheet electrode was connected to the ITO electrode, the device converted solar energy to electric energy; when an external bias voltage was applied between the two CNT sheet electrodes, it emitted light. The working mechanism of the dual-function device is summarized below.²² In the light of the schematic energy level diagram demonstrated in Fig. 3a, the photoactive layer produces excitons that are separated into electrons and holes upon connecting the middle CNT sheet and ITO electrodes under light irradiation. The electrons are transported to the ITO electrode through the ZnO nanoparticle layer, whereas the holes are transported to the middle CNT sheet electrode.

To fabricate the PC part, the CNT sheet played a crucial role in achieving high power conversion efficiency due to both high electrical conductivity and hole collection capability. The electrical resistances of the CNT layers (5 mm in width) were gradually reduced from 2.5 to 0.17 kΩ cm⁻¹ with the increasing thickness from 18 to 360 nm (Fig. S3, ESI†). A series of PC parts had been studied for photovoltaic performances with increasing CNT layer thicknesses. Fig. 3b compares the current density *versus* voltage characteristics under standard air mass 1.5 illumination (100 mW cm⁻²). The power conversion efficiencies increased from 0.78%, 1.02%, 1.28% and 1.87% to 2.07% with the increasing thickness of the CNT layer from 18, 36, 90 and 180 to 360 nm, respectively (Fig. S4, ESI†). The best performance with efficiency of 2.07% corresponds to an open-circuit voltage of 0.57 V, short-circuit current density of 9.31 mA cm⁻²,

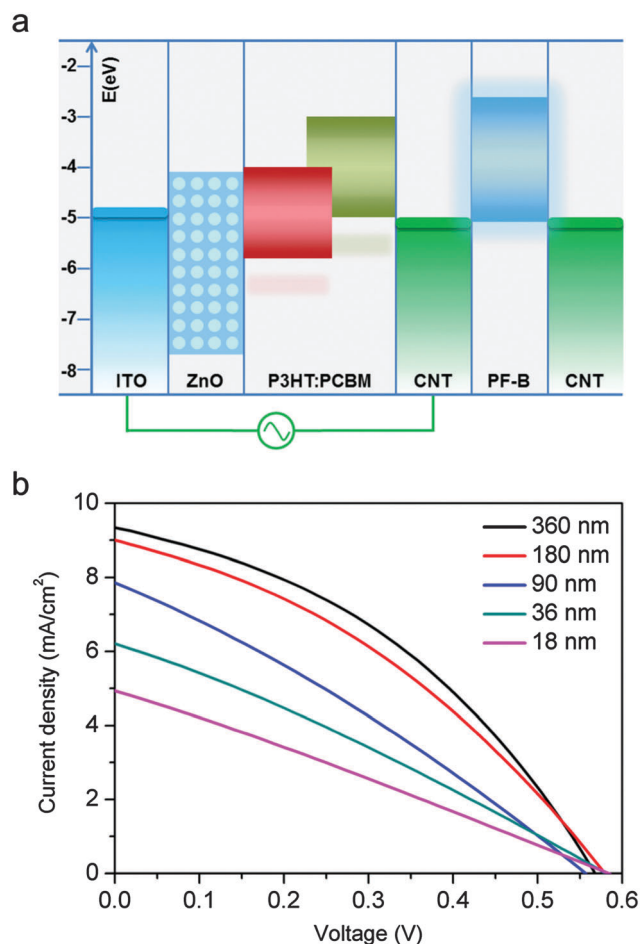


Fig. 3 (a) Schematic of the PC part consisting of the P3HT:PCBM bulk-junction layer generating electrical energy under light irradiation. (b) Current density versus voltage characteristic curves of the PC part with increasing aligned CNT layer thicknesses from 18 to 36, 90, 180 and 360 nm.

and fill factor of 39.2%. With further increase in the CNT layer thickness, the power conversion efficiency remained almost unchanged. Therefore, a thickness of 360 nm for the CNT layer is studied below unless specified otherwise. The aligned CNT sheet was also explored for its remarkable thermal and mechanical properties, and the resulting PC part without encapsulation exhibited a relatively high stability that was verified by tracing the efficiency with the time. It could be maintained by over 80% in ten days in dried air (Fig. S5, ESI†). Note that the efficiency of PC part is a little lower than the conventional polymer solar cells with the structure of ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al,²⁵ which is mainly attributed to the lack of a hole-transporting layer of PEDOT:PSS and to the Ca/Al cathode that can remarkably improve the performance.

The LE part started to work when the two CNT sheet electrodes were connected.^{9,13} It emitted light when an external bias voltage exceeded its turn-on voltage (Fig. 4a). The light-emitting PIN junction can be formed *in situ* in the emissive polymer layer without using the low work function cathode. Therefore, electrons and holes were injected into the emissive polymer layer from the two CNT sheet electrodes. Finally, the electrons and

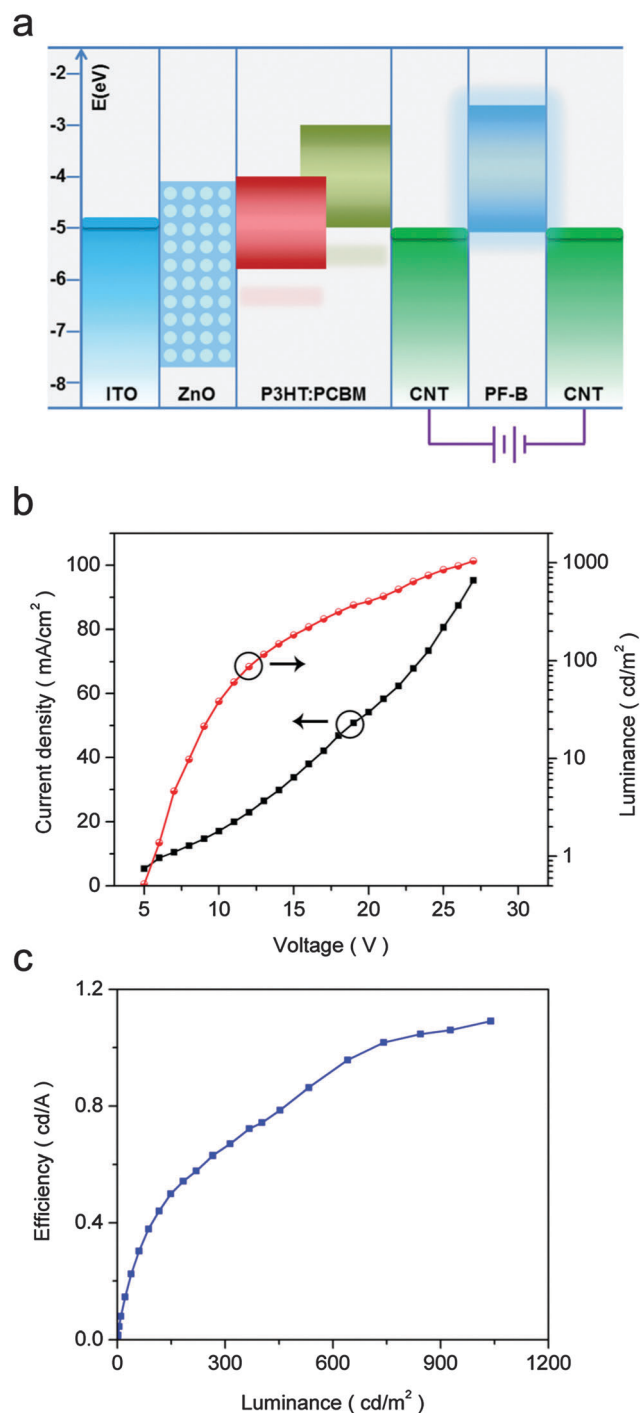


Fig. 4 (a) Schematic of the LE part consisting of the emissive polymer layer producing light under bias voltage. (b) Current density- and luminance-voltage characteristics of the LE part. (c) Current efficiency-luminance characteristics of the LE part.

holes re-combine in the emissive polymer layer and subsequently emit light.

The thickness of the CNT layer at the top was critical to achieve a high brightness, and it was important to balance the optical transmittance and electrical resistance. The optical transmittances of CNT layers had been decreased from over

91% to 77% (at a wavelength of 550 nm) with increasing thicknesses from 18 to 54 nm, respectively (Fig. S6, ESI†). In contrast, the resistances of the CNT layers decreased with increasing thickness. The highest brightness of 1040 cd m^{-2} occurred with the CNT layer thickness of 36 nm (Fig. S7, ESI†). To obtain high performance, the CNT layer with a thickness of 36 nm was used below.

Fig. 4b demonstrates the current density- and luminance-voltage characteristic curves of the LE part. This started to emit light when the voltage was higher than 5.5 V, and the brightness was increased with increasing applied voltage. The peak brightness of 1040 cd m^{-2} was achieved at 27 V. The current efficiency-luminance characteristic curve of the LE part is further shown in Fig. 4c. The highest current efficiency was 1.09 cd A^{-1} at a brightness of 1040 cd m^{-2} . The corresponding external quantum efficiency was 0.4%. Note that here the LE part emitted the light with blue-green color. According to the CIE 1931 standard color-matching functions, this can be expressed as (0.22, 0.36) regarding the x , y chromaticity coordinates (Fig. S8, ESI†). Compared with the photoluminescence spectrum of the light-emitting polymer layer (Fig. S9, ESI†), the electroluminescent spectrum of the LE part witnessed some changes, which were probably attributed to the formation of keto-defects during study.²⁶ The turn-on response of light emission from the PIN junction in the emissive polymer layer of the LE part was investigated by a pulse voltage operation (Fig. S10, ESI†). As expected, the pre-charged LE part indicated a rapid turn-on response.

In conclusion, we have successfully developed a dual-function optoelectronic device to convert solar energy to electric energy and emit light by designing a three-electrode configuration. This dual-function optoelectronic device exhibits a reasonable power conversion efficiency of 2.07% from the PC part and a high luminance of 1040 cd m^{-2} from the LE part. As it can be independently operated to generate electric energy for power and emit light for display, it is promising for a broad spectrum of applications in microelectronic and smart devices.^{27,28} This study also represents a new and general strategy in developing multi-function devices through an all-solution process.

Experimental section

Synthesis of ZnO nanoparticles

The synthesis of ZnO nanoparticles has been previously reported.¹² Briefly, zinc acetate dihydrate (0.59 g) was first dissolved in methanol (25 mL) in a 100 mL flask and then heated to 65°C under magnetic stirring. Subsequently, potassium hydroxide (0.30 g) was dissolved in methanol (13 mL) and slowly dropped into the flask during 15 min, followed by reaction for 2.5 h at 65°C . The resulting solution was cooled to room temperature and kept overnight. The supernatant was removed and the precipitant was washed with methanol for several times. Finally, methanol (1 mL), chloroform (1 mL) and *n*-butanol (14 mL) were added to disperse the ZnO nanoparticles with a concentration of 6 mg mL^{-1} . The ZnO nanoparticle solution was filtered by a poly(vinylidene fluoride) membrane (0.45 μm in diameter) prior to the use.

Fabrication of the PC part

ITO-coated glass substrates were successively pre-cleaned with deionized water, acetone and 2-propanol in ultrasonic baths each for 20 min.^{9,12} The ZnO nanoparticle layer was spin-coated onto the ITO substrate at 3000 revolutions per minute for 30 s and annealed at 120°C for 5 min. The abovementioned process was repeated three times. The P3HT:PCBM layer was spin-coated onto the ZnO layer at 1000 revolutions per minute for 60 s. The concentration of the mixture solution of P3HT and PCBM in chlorobenzene (weight ratio of 5/4) was 30 mg mL^{-1} . The resulting material was annealed at 150°C for 10 min in an argon atmosphere in the glovebox. Finally, the aligned CNT sheet was laid onto the P3HT:PCBM layer with a thickness of approximately 360 nm to complete the fabrication of the PC part.

Fabrication of the LE part

The light-emitting polymer layer was spin-coated onto the aligned CNT sheet at 3000 revolutions per minute for 60 s, followed by drying in a vacuum for 1 h. The emissive polymers were dissolved in anhydrous tetrahydrofuran, followed by addition of ETT-15 and LiTf. The weight ratios for the polymer/ETT-15/LiTf were 20/10/1, and the final concentration of conjugated polymer was 40 mg mL^{-1} . Finally, another aligned CNT sheet was attached onto the emissive polymer layer with a thickness of approximately 36 nm.

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