Flexible and wearable solar cells represent a promising direction in the advancement of next-generation energy-harvesting electronics. However, the solar cells in a planar structure cannot meet the requirements of complicated deformations. On the other hand, solar cells based on the one-dimensional structure attract increasing interest as they can stably work under both bending and twisting. Here, a family of fiber-type perovskite solar cells has been designed with impressive photovoltaic performance. They exhibit a high power conversion efficiency of 9.49% that is stable under both bending and twisting. A combination of large crystals of perovskite and aligned carbon nanotube sheets contributes to their excellent properties. Due to their unique fiber shape, they can be further woven into flexible and lightweight power textiles that are promising as the next-generation portable and wearable electronics.

Introduction

Flexible solar cells represent a promising direction in the advancement of next-generation energy-harvesting electronics. They are generally realized by coating photoactive and conducting materials onto flexible substrates such as plastic films, textile, paper and metal foil. Although great advancement has been made in flexible solar cells in the past decade with the development of transparent conductive electrodes and the use of low-temperature interface materials, there remain some intrinsic problems originating from the limitation of the conventional planar structure. For instance, a thin planar solar cell may exhibit stable power conversion efficiencies under bending/unbending, but it rapidly deteriorates in photovoltaic performance or even fails to work under more complicated deformations such as twisting, which is disadvantageous for a variety of application fields such as wearable electronics.

On the other hand, fiber-shaped solar cells attract increasing interest as, based on the one-dimensional structure, they can stably work under both bending and twisting as well as the other complex deformations. High power conversion efficiencies up to 8.45% have been achieved in liquid electrolyte systems. However, it is well recognized that sealing the thin fiber-shaped devices with liquid electrolytes is challenging. Some attempts have thus been made to develop all-solid-state dye-sensitized solar cells in a fiber shape by introducing solid electrolytes. Unfortunately, much lower power conversion efficiencies of 6.4% were observed. Several attempts had also been made to fabricate fiber-shaped polymer solar cells that were solid, but even lower power conversion efficiencies below 3.8% were produced.

Perovskite solar cells emerged as a new kind of photovoltaic devices just a few years ago and have rapidly received considerable interest due to their capability for high power conversion efficiencies. However, it is rare to make one-dimensional perovskite solar cells with high photovoltaic performances as it remains difficult to produce compact perovskite layers with large crystal sizes on the curved surfaces of fiber electrodes. On the other hand, a high coverage of an active perovskite layer is highly desirable for the effective generation and separation of excitons, while large crystals are critical for high carrier mobility and long lifetime and diffusion length. The perovskite layers are typically coated by a dip-coating process with low surface coverage and quality. Recently, a cathodic deposition process for perovskite layers with both high coverage and quality has been introduced to the fiber substrate. However, the efficiency is unsatisfactory with small crystals.

In this communication, we fabricate a new family of one-dimensional perovskite solar cells by designing a flat interface that enhances the coverage and crystal size of perovskite layers (Fig. 1a). The perovskite material was coated continuously and uniformly onto a flat one-dimensional substrate, and micrometers of crystals were formed at the flat interface. A continuous
carbon nanotube (CNT) sheet that was flexible, mechanically strong and electrically conductive had been closely attached on the perovskite layer to function as an electrode and hole extraction layer. The resulting fiber-type perovskite solar cell (FPSC) showed a high power conversion efficiency of 9.49%. It is highly flexible and demonstrates stable photovoltaic performances under both bending and twisting.

Experimental section

The FPSC was fabricated on a polyethylene naphthalate/indium tin oxide (PEN/ITO) strip that had been produced by etching with the use of 2 M HCl and Zn powder and then washed with water, ethanol and isopropanol in sequence. The strip-shaped substrate served as a transparent electrode and light was illuminated from this side. A compact blocking layer of TiO2 was deposited and annealed at 150 °C for 30 min. A PbI2/N,N-dimethylformamide solution (concentration from 200 to 450 mg mL\(^{-1}\)) was coated onto the TiO2 layer and then dried at 80 °C. The treated substrate was dipped into a CH\(_3\)NH3I/isopropanol solution (concentration in the range of 7 to 70 mg mL\(^{-1}\)), followed by annealing at 90 °C for 30 min. An aligned CNT sheet was dry-drawn from a spinnable CNT array synthesized by chemical vapor deposition, and it was further attached onto the CH\(_3\)NH3PbI\(_3\) layer. A droplet of toluene was finally dropped onto the CNT sheet, followed by annealing at 80 °C to enhance the contact between the CNT sheet and CH\(_3\)NH3PbI\(_3\) crystal. The CNT sheet was a little narrower than the underlying electrode to prevent short circuits between them. The effective area of the FPSC was calculated from the overlapped area between the two electrodes. The underlying strip with the perovskite layer was slightly larger than the CNT sheet. During the characterization of the photovoltaic performance, the edge side of the perovskite layer was covered with a black adhesive (the device size, 1 × 5 mm\(^2\)).

Results and discussion

The CH\(_3\)NH3PbI\(_3\) film was formed in a two-step sequential deposition process for the construction of the FPSC. PbI\(_2\) was first coated onto the substrate, followed by dipping into a CH\(_3\)NH3I solution. The sizes of the perovskite crystals were critical for the resulting solar cells and were controlled by varying the concentration of the CH\(_3\)NH3I solutions. The crystal sizes were ~250 nm at a 70 mg mL\(^{-1}\) solution and increased with the decrease of concentration. When the concentration was lower than 10 mg mL\(^{-1}\), the perovskite crystals were larger than 1000 nm in size (ESI Fig. S1†), e.g., 1.2 μm at 7 mg mL\(^{-1}\). The quality of the perovskite crystal was verified by X-ray diffraction. The four characteristic peaks at 14.1°, 28.4°, 31.8° and 43.2° that corresponded to the (110), (220), (310) and (314) planes in the perovskite material were clearly observed, respectively (ESI Fig. S2†). In contrast, the characteristic peak at 12.6° for the PbI\(_2\) did not appear. Importantly, the perovskite crystals could be also uniformly and densely coated on the flat one-dimensional electrode (Fig. 1b), in comparison with the low crystal coverage for a curved fiber surface (ESI Fig. S3†).

The lifetime of the charge carriers was a critical parameter to reflect the photovoltaic properties of the active material. A longer lifetime generally correlates with less defects and lower recombination in the perovskite crystal. The different sizes of perovskite crystals were thus compared for the lifetime of charge carriers by time-resolved transient absorption spectroscopy. Larger crystals obviously showed a longer lifetime, e.g., the lifetime had been lengthened by 360% when the crystal sizes were increased from 250 to 1200 nm (Fig. 2a).

In a typical perovskite solar cell, an organic hole transport layer and metal electrode are generally required at the top of the active perovskite layer. However, the organic hole transport layer or conducting polymer thin film is unstable under ambient conditions. The metal electrode also requires a high
vacuum deposition with high cost. Carbon materials as low-cost candidates have been used in Schottky solar cells, particularly, one-dimensional CNTs that exhibit a p-type conducting feature for efficient hole extraction and transport.\textsuperscript{32,33} To simplify the device structure for large-scale production, here an aligned CNT sheet was designed as both an electrode and a hole extraction/transporting layer. The aligned CNT sheet was dry-drawn from a spinnable CNT array with the synthetic details described in the ESI.\textsuperscript{†} The building CNTs were multi-walled with an average diameter of 10 nm (ESI Fig. S4\textsuperscript{†}). With an intense adhesion to the perovskite layer, the aligned CNT sheet could effectively enhance the hole extraction and transport (Fig. 1c).\textsuperscript{34,35} Stable photoluminescence measurements were made to investigate the hole extraction performance of the CNT sheet (Fig. 2b). The excited carriers would release the energy through fluorescence upon illumination of the pure CH$_3$NH$_3$PbI$_3$ layer. The significantly decreased fluorescence intensity in the CH$_3$NH$_3$PbI$_3$/CNT film indicated an effective extraction of holes, which was beneficial for charge separation.

Importantly, the vacuum deposition for the metal electrode could be eliminated here, and the corrosion of the perovskite to the metal electrode can be also prevented.\textsuperscript{31} The aligned structure was designed to extend the excellent properties of individual CNTs to a macroscopic scale, e.g., tensile strengths in the order of 10$^2$ to 10$^3$ MPa and electrical conductivities at the level of 10$^2$ to 10$^3$ S cm$^{-1}$.\textsuperscript{27} The high electrical conductivity of the aligned CNT sheet also contributed to the efficient charge carrier collection and transport process.\textsuperscript{36}

The long lifetime of the charge carriers from the micrometer-sized CH$_3$NH$_3$PbI$_3$ crystal and the effective hole extraction from the aligned CNT sheet were favorable for high photovoltaic performances. For larger crystals with a longer lifetime of charge carriers, the thickness of the photoactive layer could be increased to harvest more light. When the thickness of the perovskite layer was increased to 460 nm, most of the incident light was absorbed (ESI Fig. S5\textsuperscript{†}), and the short-circuit current density ($J_{SC}$) was also increased (Fig. 2c). Further increase of the PbI$_2$ layer thickness led to the formation of a layered structure that reduced the quality of the active layer (ESI Fig. S6\textsuperscript{†}). As a result, the photovoltaic performance of the FPSC degraded at a higher thickness such as 700 nm (Fig. 2c).

Fig. 2 Photovoltaic performances of FPSCs. (a) Comparison of time-resolved transient absorption spectra measured at 950 nm of small (250 nm) and large (1200 nm) sizes of CH$_3$NH$_3$PbI$_3$ crystals. (b) Steady-state photoluminescence spectra of a CH$_3$NH$_3$PbI$_3$ film and CH$_3$NH$_3$PbI$_3$/CNT sheet layer. (c) J–V curves of FPSCs with different thicknesses of CH$_3$NH$_3$PbI$_3$ layers. (d) J–V curves of FPSCs with different thicknesses of CNT sheets.

Fig. 3 Comparison of the power conversion efficiencies between the FPSC and other all-solid-state one-dimensional solar cells.
The photovoltaic performance of the FPSC can be further enhanced by decreasing the series resistance and enhancing the hole extraction of the CNT sheet. For instance, the electrical resistance of the CNT sheet could be remarkably decreased to tens of ohm by increasing the thickness of the CNT sheet from 20 nm to 200 nm (ESI Fig. S7†). Increasing the thickness further varied the resistance a little. With the increasing thickness of CNT sheets from 20 to 200 nm, the fill factor and current density of FPSCs were increased. However, with a further increase of the thickness to 400 nm, the fill factor was reduced a little as there existed more conjunctions among CNTs (Fig. 2d).

The FPSC had been then optimized with a 460 nm thick CH$_3$NH$_3$PbI$_3$ layer and 200 nm thick CNT layer. The resulting FPSC displayed an open-circuit voltage of 0.91 V, a short-circuit current of 15.9 mA cm$^{-2}$, and a fill factor of 0.656, which produced a power conversion efficiency of 9.49%. A moderate decrease in both $J_{SC}$ and fill factor was observed in the forward scan direction with a scan rate of 100 mV s$^{-1}$ (ESI Fig. S8†). The indistinctive hysteresis effect is ascribed to the efficient charge extraction and transport of the CNT electrode. Fig. 3 compares the photovoltaic performance of the FPSC with the other all-solid-state one-dimensional solar cells. The power conversion efficiency of the FPSC much exceeds the other one-dimensional counterparts. In addition, the FPSC also shows the highest open-circuit voltage that is important for application.

As expected, the FPSC was flexible. The power conversion efficiency was traced and compared after bending (Fig. 4a), and it had been maintained at 93% after bending for 500 cycles at a bending curvature radius of 7.5 mm. In addition, the FPSC can stably work after twisting and maintained a power conversion efficiency of over 90% (Fig. 4b). The high stability under twisting was further verified by tracing the structure evolution under a SEM (ESI Fig. S9†). Obviously, the photoactive layer had been well maintained without obvious damages in the structure. Although the increased size of perovskite crystals increased the power conversion efficiency, too large crystals would deteriorate the stability of the FPSCs due to their cracks during deforming. More efforts are underway to balance the flexibility and power conversion efficiency by optimizing them.

Another distinct advantage of this CNT sheet lay in its hydrophobic nature that prevented the infiltration of moisture into the active perovskite layer that may lead to deterioration in photovoltaic performance (ESI Fig. S10†). The main photovoltaic parameters remained unchanged after 150 h under ambient conditions without sealing (Fig. 4c).

These FPSCs were further woven into flexible and lightweight clothes, which are promising for various wearable applications. As a demonstration, five FPSCs had been integrated into a flexible belt to power a commercial electronic watch (Fig. 4d and e).

**Conclusion**

In conclusion, a new family of all-solid-state FPSCs has been fabricated with high photovoltaic performances by designing a flat interface for large perovskite crystals and attaching an aligned CNT sheet as the electrode. The FPSC produced the highest power conversion efficiency of 9.49% among the all-solid-state one-dimensional solar cells. The unique flat fiber
offered some unique and promising properties, e.g., light weight, weavability and availability of a variety of deformations including bending and twisting. This work also provides a general and effective paradigm in the development of high-performance one-dimensional photovoltaic devices.

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References

6 D. Liu and T. L. Kelly, Nat. Photonics, 2013, 8, 133–138.
26 L. Qiu, S. He, J. Yang, J. Deng and H. Peng, Small, 2016, 12, 2419–2424.