A general and effective strategy has been developed to fabricate both perovskite photovoltaic fibers and fabrics by synthesizing obelisk-like ZnO arrays to replace the TiO$_2$ layer through a mild solution process. The obelisk-like ZnO aggregates were perpendicularly grown on substrates in an aligned format and with tunable sizes, offering many advantages, such as effective penetration of a second phase into the voids with a high stability. The perovskite photovoltaic fibers and fabrics can be twisted in three dimensions without obvious damage to the structure.

Introduction

Organic–inorganic halide perovskites have emerged as a new star for the next generation photovoltaic devices.\textsuperscript{1,2} The power conversion efficiency of these compounds has displayed a sharp increase to approximately the same as crystal silicon-based solar cells over past five years.\textsuperscript{3,4} In particular, the intrinsic properties, including solid state and easy processing, offer promising applications for flexible and wearable electronic devices that represent a rapidly growing direction in multidisciplinary fields. However, the requirement of annealing at high temperatures for the compact and mesoscopic TiO$_2$ layer in the typical structure has largely limited the application of perovskite solar cells, \ie the commonly used flexible polymer substrates cannot survive thermal treatment at high temperatures.\textsuperscript{5–14} A low temperature solution process for the preparation of the TiO$_2$ compact and mesopore layer is also promising for efficient perovskite solar cells, although most of them were fabricated on rigid glass substrates.\textsuperscript{15–17} In addition, the available flexible perovskite solar cells appear in a planar structure that can be typically bent along one direction but cannot be twisted in three dimensions.\textsuperscript{18} As a result, it is not effective for them to be used on soft and curved substrates as well as for wearable applications. Furthermore, although the flexible planar perovskite solar cells can be made to be thin, they are still relatively heavy and large, and cannot be effectively integrated into wearable and micro-electronic devices. Therefore, it is necessary to develop lightweight, three-dimensional flexible perovskite photovoltaic devices through low-cost and highly-efficient fabrication processes.

Herein, a general and effective strategy has been developed to fabricate both perovskite photovoltaic fibers and fabrics by synthesizing obelisk-like ZnO arrays to replace the TiO$_2$ layer through a mild solution process. Unlike traditional dye-sensitized and quantum-dot solar cells with similar structures, the perovskite layer possesses a higher light absorbing efficiency and charge carrier mobility, so the thickness of the solid-state cell can be made thinner, which is beneficial for producing flexible devices. Further, the obelisk-like ZnO aggregates are perpendicularly grown on substrates in an aligned format and with tunable sizes, providing many advantages, such as effective penetration of a second phase into the voids and rapid charge transport along their axes, which are further promoted by the high specific surface area. As a result, both the perovskite photovoltaic fibers and fabrics demonstrate high power conversion efficiencies. The perovskite photovoltaic fibers and fabrics can be twisted in three dimensions without obvious damage to the structure, and the power conversion efficiencies varied by 7% after deforming for 200 cycles.

Experimental section

Growth of the ZnO nano-obelisk array

A KOH/methanol solution (0.487 g in 23 mL) was dropped into a zinc acetate/dehydrate methanol solution (0.979 g in 42 mL) with stirring at 63 °C. After reacting for 2.5 h, the solution was cooled down to room temperature and left to stand overnight.
prior to centrifugation. The centrifuged ZnO nanoparticles (0.356 g) were re-dispersed in a solvent mixture of chloroform (1.5 mL), isopropanol (1.5 mL) and methanol (25 mL). A substrate was then inserted into the resulting solution, followed by drying at room temperature. The synthesis of the ZnO nano-obelisks was carried out in an aqueous solution containing 0.03 M Zn(NO₃)₂·6H₂O, 0.025 M (CH₂)₆N₄ and 0.005 M polyethyleneimine (Mₜw = 1200 g mol⁻¹) at a temperature range of 50 to 90 °C and a time range of 5 to 120 min. The products were rinsed with deionized water three times and dried at 90 °C.

### Fabrication of a fiber-shaped PSC

A stainless steel wire (diameter of 0.127 mm) was sequentially washed with acetone, isopropanol and deionized water under ultrasonic treatment for 10 min each. The synthesis of CH₃NH₃I is described in the ESI.† After being modified with the aligned ZnO nano-obelisk array on the surface, the steel wire was inserted into a 1 M PbI₂/dimethyl sulfoxide solution for 30 min. A stainless steel wire (diameter of 0.127 mm) was sequentially washed with acetone, isopropanol and deionized water under ultrasonic treatment for 10 min each. The synthesis of CH₃NH₃I is described in the ESI.† The resulting fiber was soaked in a CH₃NH₃I/ isopropanol solution (10 mg mL⁻¹) for 10 min and annealed at 80 °C for 30 min. After cooling to room temperature, it was dropped into a hole-transporting material solution containing 2,2',7,7'-tetraakis[N,N-para-dimethoxyphenyl-amine]-9,9-spirobifluorene (61.4 mM), lithium bis(trifluoromethylsulfonyl)imide (26 mM), and 4-tert-butylpyridine (55 mM) in a mixed solvent system of chlorobenzene and acetonitrile (volume ratio of 20/1). A transparent CNT sheet was finally wrapped around the resulting wire to produce a fiber-shaped PSC. The preparation of the CNT sheet is described in the ESI.†

### Results and discussion

The aligned obelisk-like ZnO arrays were synthesized through a chemical bath deposition method. Briefly, a layer of ZnO nanoparticles (5 nm in diameter) was dip-coated on the desired substrate, such as a stainless steel wire, as nucleation sites (Fig. S1 and S2†). The ZnO nano-obelisks were then perpendicularly grown on the substrate at low temperatures (60–100 °C) in an aqueous solution containing Zn(NO₃)₂·6H₂O, (CH₂)₆N₄ and polyethyleneimine (PEI). The related reactions during the growth are listed below.¹⁷

\[
(CH₂)₆N₄ + 6H₂O \rightarrow 6HCHO + 4NH₃ \quad (1)
\]

\[
NH₃ + H₂O \rightarrow NH₄⁺ + OH⁻ \quad (2)
\]

\[
Zn^{2+} + 2OH⁻ \rightarrow Zn(OH)₂ \quad (3)
\]

\[
Zn(OH)₂ → ZnO + H₂O \quad (4)
\]

Fig. 1 shows a ZnO nano-obelisk array radically grown on a stainless steel wire with a number density of ~10¹⁰ cm⁻² on the surface. The diameters of the nano-obelisks fluctuated around 150 nm at the bottom and gradually decreased to ~70 nm along the axis before a sharp tip. The ZnO nano-obelisks were stably anchored on the substrate even after bending 1000 times.

Several factors exert significant impacts on the formation of the ZnO nano-obelisks. The ZnO nanoparticles act as a seed layer to initiate the radical growth of the nano-obelisks.¹⁸ In the absence of the nanoparticles, ZnO aggregates were sparsely strewn over the substrate rather than densely and perpendicularly aligned under the same growing conditions (Fig. S3†). PEI is also indispensable for a longer and thinner array. Irregular larger aggregates rather than aligned ZnO nano-obelisks were produced without the space limitation of growth with PEI (Fig. S4†).¹⁹ Thermodynamically, the crystals were inclined to grow preferentially from the high energy crystal plane, i.e. the (0002) plane in the ZnO material.²⁰ PEI can be absorbed onto the nonpolar side facets, making the (0002) plane favorably exposed in the solution, which was corroborated by the high-intensity (0002) diffraction peaks in the X-ray diffraction (XRD) patterns.¹⁹

Besides the ZnO seed particles, the growth of the ZnO nano-obelisks was also affected by time and temperature. Fig. S5† traces the morphology evolution of the ZnO nano-obelisks during growth. ZnO buds sprouted from the seed layer in the first 10 min. The “buds” then evolved into a nano-array in the following 20 minutes (Fig. S6†). Afterwards, the ZnO nano-obelisks grew longer with the increasing time (Fig. S7†). The temperature kinetically facilitated the growing process, and a higher temperature produced longer ZnO nano-obelisks (Fig. S7–S9†). The length distributions of the ZnO nano-obelisks grown for 90 min at different temperatures is shown in Fig. S10†. In the present study, the ZnO nano-obelisks could be obtained within a temperature window of between 60 and 90 °C. As expected, the diffraction intensities were enhanced with increasing temperature, indicating that the ZnO nano-obelisks formed better crystal structures at higher temperatures. At a lower temperature, such as 50 °C, and a higher temperature, such as 100 °C, no ZnO nano-obelisks were observed (Fig. S11 and S12†). This phenomenon
may be explained by the inhibition of nucleation and growth at lower temperatures and “Ostwald ripening” of the seed layer that aggregates into larger particles at higher temperatures. Importantly, the growth of nano-obelisks was imperative to the substrate and could be realized on various curved and planar substrates, such as titanium wire, copper foil and fluorine doped tin oxide glass (Fig. S13†). Unlike the previously required high temperature annealing processes for TiO2 that might oxidize the metal substrate and deteriorate the electrode performance by reacting with the metal oxide blocking layer, this mild process does not damage the properties of substrates.21

The crystallinity of the nano-obelisks was analyzed by XRD spectroscopy and transmission electron microscopy (TEM). The XRD pattern shows strong and sharp characteristic diffraction peaks that indicate a hexagonal wurzite crystallite (Fig. S14†). The higher peak at 34.4° corresponds to a (0002) plane, suggesting that the nano-obelisks were grown along the [0001] direction perpendicular to the substrate.22 The TEM image and corresponding electron diffraction pattern in Fig. S15† also back up this conclusion. The formation of sharp tips on the ZnO nano-obelisks is related to the variation in Zn2+ concentration during growth. When the Zn2+ ions are depleted in the solution, the crystal growth tends to slow down, which differentiates the growing rates between the plane center and boundary. A sharp tip is formed when the center grows faster than the boundary with increasing growth time (Fig. S16†).

The unique one-dimensional structure and mild growing conditions make the ZnO nano-obelisks applicable in flexible photovoltaic devices. A fiber-shaped perovskite solar cell (PSC) was then fabricated using the aligned ZnO nano-obelisks as an effective electron transport layer. The light-harvesting perovskite and hole conductors were successively impregnated on the ZnO nano-obelix scaffold that was prepared on a steel wire. Carbon nanotube (CNT) sheets, which are conductive and transparent, were wrapped on the outside as the back contact electrode (Fig. 2a and S17†).24

The CH3NH3PbI3 perovskite layer was prepared through a two-step dip-coating process. PbI2 was first dissolved in dimethyl sulfoxide and then dip-coated onto the ZnO nano-obelix array to form a thin and dense layer (Fig. S18†). The as-prepared CH3NH3PbI3 crystals typically had a cubic structure and their sizes were decreased when CH3NH3I concentrations were increased from 4 to 10 mg mL−1 (Fig. S19†, 2c and 2d).26 It should be noted that the size of CH3NH3PbI3 should be compatible with the ZnO scaffold. When the CH3NH3PbI3 crystals were too large, the ZnO nano-obelisks were prone to collapsing, resulting in short circuits and poor performances of the solar cell (Fig. S20†). Therefore, in the present study, a uniform CH3NH3PbI3 capping layer was prepared from a 10 mg mL−1 CH3NH3I solution and infiltrated into the voids of the ZnO obelix scaffold (Fig. 2c and d). The complete structure of this perovskite solar cell fiber is shown in Fig. S21† with a thickness of ~150 nm for the perovskite capping layer and 350 nm for the hole transport layer.

Fig. 3a displays the current density–voltage (J–V) curves of fiber-shaped PSCs containing ZnO nano-obelisks with different lengths. The comparison revealed that the 700 nm ZnO nano-obelisks provided the solar cell with the highest power conversion efficiency of 3.8%, which was due to a compromise between the surface area and the charge recombination. This value is higher than the value for perovskite solar cells based on ZnO nanorods fabricated on planar polymer substrates, which exhibit a power conversion efficiency of 2.61% with an open-circuit voltage of 0.8 V, short-circuit current density of 7.52 mA cm−2 and fill factor of 0.43.29 Longer obelisks with higher surface areas can absorb more perovskite materials but they increase the pathways for charge transport with more charge recombination. In contrast, shorter obelisks can reduce the charge recombination while also decreasing the surface area.

To highlight the merit of the nano-obelix morphology, a ZnO seed layer and a nanorod array were also introduced as electron transport layers to fabricate fiber-shaped PSCs under the same conditions. As a small amount of perovskite was attached to the ZnO seed layer, the resulting PSC produced a much lower Jsc value of 3.72 mA cm−2 and a power conversion efficiency of 0.98% (Fig. S22 and S23†). In the case of the ZnO nanorod array, the perovskite could not be fully infiltrated into the voids, which engendered a severe charge recombination, leading to an inferior power conversion efficiency of 1.0% (Fig. S24 and S25†).27–29 Due to a coaxial structure, the photovoltaic performance of the fiber-shaped PSC was insusceptible to the angle of incident light (Fig. 3c). As the ZnO nano-obelisk array was firmly anchored on the fiber substrate, the fiber-shaped PSC was flexible and could be bent without fatigue. The power conversion efficiency was
maintained at 93% after bending for 200 cycles (Fig. 3d). The stability in the power conversion efficiency upon bending is comparable to the flexible planar counterpart, where a decrease of ~7% was observed. In particular, the fiber shape offered a unique capability for three-dimensional deformations, such as twisting, that are generally unavailable for conventional planar solar cells. The power conversion efficiency was maintained at 84% after twisting with a twisting angle of 30° (Fig. 3e and f). Note that here the piezoelectric dipole may also slightly contribute to enhancing the power conversion efficiency of the fiber-shaped perovskite solar cell based on the ZnO array under deforming conditions due to the increased built-in electric field that enhanced the charge separation and transport.

Based on a similar strategy, a ZnO nano-obelisk array was also grown on a fabric substrate, such as a steel fabric (Fig. 4). As a result, an all-solid-state PSC fabric with a stable performance can be developed through the method described above (Fig. S26†). As expected, this photovoltaic fabric was also flexible and could be bent for hundreds of cycles without obvious damage to the structure.

**Conclusion**

In conclusion, we have synthesized a new family of obelisk-like ZnO arrays through a low-temperature and solution-based process. The mild growing conditions make the ZnO nano-obelisk array compatible with various flexible polymer substrates that are highly desired for flexible photovoltaic devices. As a promising application, the ZnO nano-obelisk array has been introduced as the electron transport layer to make novel PSCs in both fiber and fabric formats. This work also provides a general and effective strategy for the structure control of nanomaterials for electronic and energy devices.

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