**Cellulose Paper** 



# Flexible and Biocompatibility Power Source for Electronics: A Cellulose Paper Based Hole-Transport-Materials-Free Perovskite Solar Cell

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Flexible, biocompatible, and light-weight power sources are urgently required due to their promising application in wearable electronics. Organic-inorganic hybrid lead halide perovskite solar cells (PSCs) with their impressive efficiency and scalable processing capability have emerged as promising candidates for efficient and reliable power sources for wearable electronics. However, the progress in developing low-cost and efficient flexible PSCs has been confined to Poly(ethylene terephthalate) or metal foil substrates and difficulty to design PSCs on other easily accessible low-cost substrates such as cellulose paper. Herein, the authors report the hole transport material (HTM)-free flexible PSCs fabricated on abundant, low-cost, and biocompatible cellulose paper substrate for the first time. The highest PCE of 9.05% for the paper based flexible HTM-free PSC is achieved and the device could maintain over 75% of its initial PCE after 1000 bending cycles, demonstrating good stability against bending deformation. Our findings provide an avenue to fabricate reliable power source for wearable electronics.

Owing to the rapid growth of portable and wearable consumer electronics, the sustainable mobile energy sources have been extensively explored to fulfill the increasing demands from intelligentized modern life.<sup>[1–3]</sup> However, the most commonly utilized energy units, such as silicon cells and capacitors, are normally fragile, heavy, and toxic to meet the particular requirements of flexible electronics, which precludes them from being commercialization.<sup>[3,4]</sup> Therefore, in order to circumvent the aforementioned issues, light-weight power sources with mechanical flexibility are highly demanded.<sup>[5]</sup> Until now, continuous developments of exploring the interface engineering and novel device architectures have nourished progress in building better

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power source. Among these energy devices, organic-inorganic hybrid lead halide perovskite solar cells (PSCs) have attracted great attention due to their impressive power conversion efficiency (PCE) of 22.17% on rigid substrate and compatibility to low-temperature solution process.<sup>[6–10]</sup> Additionally, with characteristics of low-cost and large-area fabrication processes, flexible PSCs on biocompatible substrates become the most promising power source for wearable electronics.<sup>[11,12]</sup>

By virtue of low-temperature and solutionprocess, substantial efforts have been directed at investigating flexible PSCs based on plastic sheets (e.g., PET) or conductive metal foils (e.g., titanium).<sup>[13,14]</sup> For example, You et al. demonstrated flexible PSCs (ITO/PEDOT: PSS/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3-x</sub>Cl<sub>x</sub>/PCBM/Al) with a PCE of 9.2% on PET substrate through the

low-temperature spin-coated method.<sup>[15]</sup> Wang et al.<sup>[13]</sup> fabricated flexible PSCs on conductive titanium metal foil substrate and a PCE of 8.31% was achieved, which is the highest PCE for TiO<sub>2</sub> nanotube based PSCs. Nevertheless, it may be inevitable to cause drawbacks, for example, the generation of cracks in PSC based on plastic or conductive metal foils, decreasing of PCE under repeatedly bending condition.<sup>[16–18]</sup> Moreover, the biocompatibility of adopted substrate is an indispensable requirement for wearable electronics as it may contact our skin directly. Hence, developing alternative flexible and biocompatible substrates for wearable PSCs is urgent and strongly desirable.

Cellulose paper, as typical stationery invented 2000 years ago in China,<sup>[19]</sup> possesses admirable properties such as flexible, biocompatible, light-weight, low-cost, and accessibility in terms of roll-to-roll large-area, making it a very promising alternative to conventional flexible substrate.<sup>[20,21]</sup> What's more, previous reports prove that the biocompatibility of cellulose paper is better than PET.<sup>[22,23]</sup> Based on these advantages, cellulose paper has been successfully introduced into several kind of functional devices such as displays,<sup>[24]</sup> and biosensors.<sup>[25]</sup> Particularly, paper based solar cells have received a great deal of attention because they are considered to be the ideal flexible and portable power sources for wearable electronic commodities.<sup>[26,27]</sup> For instance, a PCDTB/PEDOT organic solar cell with PCE of 5.88% based on transparent paper substrate with good transparency was reported by Fang et al.<sup>[28]</sup> Voggu et al.<sup>[26]</sup> successfully fabricated a CuInSe<sub>2</sub> nanocrystal solar cell with the structure of bacterial cellulose/gold/CuInSe<sub>2</sub>/ZnO/ITO, but with PCE of as low as 2.25%. Despite these inspired works have been made to investigate paper based solar cell, it still remains challenges to design PSC based on cellulose paper serving as power source.

In addition, the stability of PSCs is still unsatisfactory that is the main bottleneck impending their commercialization due to the utilization of unstable and expensive organic hole transport materials (HTMs), such as PEDOT:PSS and poly-3-hexylthiophene (P3HT).<sup>[29]</sup> Therefore, wearable PSCs that are free of organic HTMs are also highly demanded. Fortunately, the unique ambipolar property of perovskite material could serve as both light harvester and hole transporter, providing the possibility for fabrication HTM-free PSCs.<sup>[30]</sup> Mei et al. have been fabricated a HTM-free, fully printable carbon (C) based mesoscopic PSC, which could be stable for >1000 h in ambient air under full sunlight and the PCE of 12.8% is achieved.<sup>[31]</sup> Given such features of inherently water-resistant, stable, lowcost, and inert to ion migration originating from perovskite and metal electrodes, C is regarded as the most promising hole extraction electrode material.[32,33]

Here, we report HTM-free, biocompatible, and flexible PSCs fabricated on low cost and abundant cellulose paper, aiming to inspire its potential application for wearable electronics. In this work, C was utilized to modify cellulose paper via a facile screenprinted process which is described and schematically shown in Figure S1, Supporting Information. The obtained flexible and conductive C-paper was used as substrate, where CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> (MAPbI<sub>3</sub>) was directly deposited with a two-step sequential vacuum thermal evaporation strategy, as we have demonstrated.<sup>[34]</sup> To the best of our knowledge, the flexible, biocompatible, and wearable HTM-free PSC with cellulose paper substrate was fabricated for the first time, and the highest PCE of 9.05% was successfully realized. The overall layout of this device is shown in Figure S2, Supporting Information. With the low cost, biocompatibility, and flexible paper as substrate, such PSCs will not only have extensive applications in wearable and portable electronics, but also render a green and alternative approach to traditional PSCs fabrication methods. The layer device architecture of the designed paper based HTM-free PSC is shown in Figure 1a.

To begin, the typical physical properties of C-paper electrode that are important for wearable PSC application were checked. The hydrophobic property is firstly evaluated by measuring the water contact angle, as shown in Figure S3, Supporting Information. When a droplet of water was dipped onto the C-paper electrode with time of 0, 60, and 120 s and the contact angles were 144.3°, 144.0°, and 143.8°, respectively, implying its excellent hydrophobic peculiarity. The good hydrophobic C-paper electrode, we believe, is able to prevent the sweat from destroying the MAPbI<sub>3</sub> perovskite when the resulting C-paper PSC is worn on human body. Then, the conductivity of the C-paper electrode is investigated and the sheet resistance is examined using a four probe station, which is measured to be 14.20  $\Omega\,\text{sq}^{-1}$  , comparable with the FTO/glass substrate (14.69  $\Omega$  $sq^{-1}$ ), as shown in Figure S4, Supporting Information. Moreover, a commercial red LED connected in series with two pieces of C-paper electrode was successfully lit up by a 3.7 V battery, further implying its great conductivity, as shown in Figure S5, Supporting Information, Specifically, a two-step sequential vacuum thermal evaporation strategy was adopted to grow high quality pinhole-free MAPbI3 film with great reproducibility. The photograph of MAPbI<sub>3</sub> film grown on cellulose paper substrate is shown in Figure S6, Supporting Information. The color changes from yellow (Figure S6a, Supporting Information) to dark brown (Figure S6b, Supporting Information) indicates the successful formation of MAPbI<sub>3</sub>. The crystallinity of MAPbI3-paper substrate was investigated as shown in Figure S7, Supporting Information. the crystallinity of MAPbI<sub>3</sub> film grown on paper substrate was investigated with X-ray diffraction (XRD) where the obviously characteristic peaks at 14.08°, 28.40°, 31.84°, and 43.21° are assigned to the (110), (220), (310), and (330) planes of orthorhombic crystal of MAPbI<sub>3</sub>, respectively. To characterize the optical property of MAPbI<sub>3</sub> film, a FTO/glass was used as the substrate while keeping the other conditions same for the control experiment. The optical absorption spectrum demonstrates a high light harvesting capability of MAPbI<sub>3</sub> spanning the visible to the near-infrared spectrum (Figure S8, Supporting Information).

As the opaque C-paper as electrode hinders the light absorption, a transparent top electrode is required to replace conventional metallic counter electrode. In present work, an



Figure 1. a) Planar layer device architecture of the paper based HTM-free PSC and (b) corresponding energy level diagram.



ultrathin Cu and Au bimetallic layer with thickness of 1 and 6 nm, respectively was deposited consecutively to form the transparent top electrode. The transmittance spectrum of such Cu/Au transparent electrode deposited on FTO/glass substrate was measured (Figure S9, Supporting Information), and an average transmittance of 61% is obtained from 300 to 800 nm. Furthermore, optical images of transparent electrode grown on paper and FTO/glass are shown in Figure S10 and S11, Supporting Information, implying their acceptable transparency.

The device architecture of resultant flexible paper based HTM-free PSC is schematically illustrated in Figure 1a. From bottom to top, the device has a paper/C/MAPbI<sub>3</sub>/C<sub>60</sub>/BCP/Cu/ Au layered structure, where BCP stands for bathocuproine. In this device, C<sub>60</sub> and BCP are served as an electron transporting layer and a hole blocking layer, respectively. As for PSCs, appropriate alignment of energy bands between the carrier transport layer and MAPbI<sub>3</sub> active layer is required to achieve high efficiency. The energy level diagram and the transfer of charge carriers are exhibited in Figure 1b, guaranteeing the high photovoltaic performance of as-designed paper based PSC. Under light illumination, photogenerated electrons and holes are produced in the conduction band (CB) and valence band (VB) of MAPbI<sub>3</sub>, respectively. The electrons in the CB of MAPbI<sub>3</sub> are subsequently injected into C<sub>60</sub>, while the photogenerated holes in the VB are extracted by C-paper electrode.

The surface morphology of each layer is observed by scanning electron microscope (SEM), as presented in **Figure 2**. It could be seen that the porous network of numerously intertwined cellulose fibers composed the paper substrate (Figure 2a). In addition, the cross-section SEM image of the bare paper is shown in Figure S12, Supporting Information, and the thickness is

around 150 µm. As seen from Figure 2b, the surface of C-paper electrode is still rough and the sheet resistance is large  $(43 \Omega \text{ sq}^{-1})$ . However, after polished with an agate lapping hammer, a smoother surface with enhanced conductivity is obtained (Figure 2c). The compact and dense C layer completely covers the paper substrate with decreasing resistance of 14.2  $\Omega$  sq<sup>-1</sup>, which is critical for the subsequent uniform growth of perovskite film. In addition, atomic force microscope (AFM) analyses of the C-paper electrode surfaces before and after polishing are also presented. As shown in Figure S13, Supporting Information, the root-mean-square roughness (RMS) of C-paper electrode before and after polishing is 854.7 and 99.5 nm, respectively. The polishing processes could make the surface of C-paper electrode much smoother. As observed clearly in Figure 2d, the MAPbI<sub>3</sub> deposited on C-paper electrode exhibits a fully covered surface morphology with densely packed grains. The smooth C layer shows enhanced interface contact with MAPbI<sub>3</sub>, which could improve the device performance. Then, the C<sub>60</sub> layer (Figure 2e) and BCP hole blocking layer (Figure 2f) were sequential deposited through same vacuum thermal evaporation method.

The inset of **Figure 3**a shows the image of an actual bent paper based HTM-free PSC, which possesses super flexible feature and exhibits the potential for wearable solar power source. Figure 3a, b present representative cross-sectional SEM image of the layered device structure. As seen, it is difficult to distinguish clearly the layered structure due to the special interstitial and hierarchic structure of flexible paper substrate when cut off compared with common used FTO/glass substrate.

The steady-state photoluminescence (PL) spectra of the MAPbI<sub>3</sub>,  $C/MAPbI_3$ , and  $MAPbI_3/C_{60}$  were measured to



**Figure 2.** Surface SEM images of the layers during the different fabrication processes of paper based HTM-free PSC. a) Pure bare paper substrate. b) C-paper electrode without and (c) with polishing. d) MAPbI<sub>3</sub> perovskite layer. e)  $C_{60}$  layer. f) BCP layer.





**Figure 3.** a,b) Cross-section SEM images of paper based HTM-free PSC. Inset of (a) is an optical image of an actual bent device.

confirm the efficient charge transfer from the perovskite light absorbing layer to the transport layer, as shown in **Figure 4**a. The excitation light enters the device from the paper modification side with an incidental angle of  $30^{\circ}$  and PL emission signal is collected from the same side, as the paper substrate is totally opaque. A clear PL quenching behavior by both introduction of C and C<sub>60</sub> was observed with respect to the pristine perovskite film, indicating that the efficient charge carries extraction ability of C and C<sub>60</sub> from the perovskite layer. To further confirm these charge extraction processes, time-resolved photoluminescence (TRPL) spectrum was also measured as shown in Figure S14, Supporting Information. The fitted parameters of TRPL were listed in Table S1, Supporting Information. For the perovskite layer, a photocarrier lifetime of 87.2 ns was obtained. When the



**Figure 4.** a) The steady-state photoluminescence spectra of MAPbI<sub>3</sub> (black curve), C/MAPbI<sub>3</sub> (red curve) and MAPbI<sub>3</sub>/C<sub>60</sub> (blue curve) on paper substrate. b) *J*-V characteristic curves of the best performance of paper based HTM-free PSC with forward and reverse scanning directions under a solar simulator irradiation of 95 mW cm<sup>-2</sup>. The inset table shows the photovoltaic performance parameters,  $J_{sc}$  (mA cm<sup>-2</sup>), PCE (%),  $V_{oc}$  (V), and FF (%). c) The corresponding EQE spectrum. d) *J*-V curves of the device with different bending cycles.

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perovskite layer is deposited onto C or C<sub>60</sub>, the PL lifetime is reduced clearly. For the C/MAPbI<sub>3</sub>, the carrier lifetime decreases to 41.4 ns, and the lifetime of MAPbI<sub>3</sub>/C<sub>60</sub> further drops to 24.8 ns, indicating that both C and C<sub>60</sub> film could effectively extract carriers from photoexcited perovskite film. The current density-voltage (*J*-*V*) curves and corresponding external quantum efficiency (EQE) of the best performance PSC are plotted in Figure 4b,c. As seen, the best performing device demonstrated a maximum PCE of 9.05% with a short circuit current density (*J*<sub>sc</sub>) of 14.42 mA cm<sup>-2</sup>, an open circuit voltage (*V*<sub>oc</sub>) of 0.84 V, and a fill factor (FF) of 70.98%.

Specifically, unlike the traditional PSCs fabricated on FTO/glass, the light irradiates on paper based HTM-free PSC from the top transparent electrode side and the average transmittance from 300 to 800 nm is 61%, which is similar to semitransparent perovskite solar cell and the highest reported PCE is only 10.3% at an average visible transmittance (AVT) of 38%.<sup>[35]</sup> If the AVT increases to 46%, the PCE is only as low as 3.55%.<sup>[36]</sup> The EQE of the champion device was measured and the integrated current density value calculated from the EQE spectra is 14.51 mA cm<sup>-2</sup>, which is well consistent with the  $J_{sc}$  value obtained from the J-V scanning curve (Figure 4c). To investigate feasibility of the paper based HTM-free PSC utilized as a flexible power source for practical application, the operational stability against repeated mechanical bending with a radius of curvature (*R*) of 6 mm was

evaluated. The *J*-*V* characteristics were measured after several bending cycles of the best performance device, as shown in Figure 4d. As seen, with the bending number increased, the *J*-*V* curve moves inwards, indicating that the most affected parameter after bending is FF. The reason is that, during repeating bending, micro-sized cracks could be generated at the interfaces between different layers, increasing the device series resistance, and further leading to the decrease of FF.

Then, the performance reproducibility of the resultant paper based HTM-free PSC was checked by measuring 20 control devices. As shown in Figure 5a, the statistics results exhibit that the average PCE of the 20 cells is 7.21%, with an average  $V_{\rm oc}$  of 0.82 V,  $J_{\rm sc}$  of  $12.05 \text{ mA cm}^{-2}$ , and FF of 61.32%. Additionally, the PCE property dependence on bending cycles of the champion device is presented in Figure 5b. After 1000 bending cycles, the  $V_{oc}$ reduces from 0.85 V to 0.77 V with  $J_{sc}$ decreasing rom 14.42 to  $13.63 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ , and FF dropping from 70.98% to 56.21%. As a result, the PCE decreases from 9.05% to 7.01%. These results demonstrate that such designed flexible paper based HTM-free PSCs possess acceptable bending durability and offer the potential for development shapeconforming and biocompatibility power

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**Figure 5.** a) Photovoltaic parameters of  $V_{oc}$ , FF,  $J_{sc}$ , and PCE presented with box diagrams for 20 devices. b) Plot of photovoltaic parameters as a function of bending cycles. c) Optical image of paper based HTM-free PSC attached on the wrist and d) bent with *R* of 6 mm.

source. As expected, the obtained paper based device could be worn onto human wrist to harness solar energy to power electronics, verifying the wearability of our paper based HTMfree PSC and proving the feasibility of application in wearable electronics (Figure 5c). As shown in Figure 5d, the paper based device remains stability under bended with *R* of 6 mm, which demonstrated that a reliable super flexible and wearable power source based on paper substrate could be realized.

In summary, a flexible and biocompatible paper based HTM-free PSC as a proof of concept was successfully demonstrated for the first time, which provides a promising approach to portable and wearable power source. Such HTM-free PSC is fabricated on ordinary cellulose paper with a transparent Cu/Ag top electrode and a champion PCE of over 9% is successfully realized. These devices also exhibit superb stability against bending deformation and maintain over 75% initial PCE even after 1000 bending cycles with the R of 6 mm, which proves an ultimately high fatigue resistance to become an effective power source for wearable device. The lightweight and super flexibility of paper based devices provide a solution in reducing their installation cost, and open new venues for applications in future wearable devices. Most importantly, efforts are being devoted to further increasing the PCE of paper based PSC, so that it may meet the practical requirements for wearable power source.

#### **Experimental Section**

*Synthesis of*  $CH_3NH_3I$ : In brief, hydroiodic acid (32.3 mL, 45 wt% in water) was added to methylamine (30 mL, 40% in methanol) in a round bottom flask in ice-water bath for 2 h under stirring, followed by heated in a rotary evaporator at 60 °C for 30 min to remove the solvent. The obtained  $CH_3NH_3I$  was firstly thoroughly washed with ethanol and then with diethyl ether, repeating this process three times. Finally, the products were dried in a vacuum oven at 60 °C for 8 h.

Preparation of C-Paper Electrode Through Screen-Printed Strategy. The processes of the screen-printed were shown in Figure S1, Supporting Information. Firstly, the screen printing plate which makes of a piece of porous, finely woven nylon mesh stretched over a frame of aluminum is customized after obtained from Henglitong company, Jinan, China. The pattern of screen printing plate was designed with Adobe illustrator CS6 software. A stencil is made on the screen which is formed by stapling mesh and masking to a frame, followed by placed atop the paper substrate fixing on the desktop.

Then carbon ink is added at one end of screen and a squeegee is used to press down and draw carbon ink to the other end. After that, the screen printing plate is taken away from the paper substrate and the print is checked. The above operation is repeated for three times. Finally, the obtained C-paper electrode was dried in ambient air at 80 °C.



Fabrication of Paper Based HTM-Free PSC: Initially, the paper substrate was cut into the shape of rectangle with length of 1.7 and 1.8 cm. As shown in Figure S2, Supporting Information, C-paper electrode is obtained with screen-printed method on part A, while part B maintains pure paper. Subsequently, part A was polished with an agate lapping hammer to make the surface smooth and shiny. Then, PbI<sub>2</sub> powders were used to form PbI<sub>2</sub> film (150 nm) onto obtained C-paper substrate via vacuum vapor phase deposition (evaporation electric current: 25 A; Chamber pressure:  $\approx 8 \times 10^{-6}$  mbar) with the deposition rate of < 0.1 Å s<sup>-1</sup>. The thickness of PbI<sub>2</sub> film, which is detected by the film thickness meter in the chamber, could be controlled by the evaporation time. The obtained PbI2 film modified C-paper substrate was immobilized onto the home-made box making of glass sheets which was around 2 cm above the CH<sub>3</sub>NH<sub>3</sub>I powders. Then the box was put into a quartz tube furnace under the temperature of 120 °C for an hour to form the MAPbI<sub>3</sub> perovskite film (300 nm) and the environmental humidity was controlled under 25%. The color changes from yellow to dark brown indicating the formation of MAPbI<sub>3</sub> perovskite. After growth of a  $\approx$  300 nm thick perovskite film, layers of C<sub>60</sub> (30 nm) and BCP (5 nm) were obtained with the same vacuum vapor phase deposition protocol. At last, the Cu and Au layer with the thicknesses of 1 and 6 nm, respectively, was thermally evaporated on the BCP film at  $1 \times 10^{-6}$  Torr in a vacuum deposition chamber to form the Cu/Au transparent electrode.

### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

#### **Keywords**

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