



# Efficient hole-conductor-free, fully printable mesoscopic perovskite solar cells with carbon electrode based on ultrathin graphite



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## ABSTRACT

Ultrathin graphite has been applied in hole-conductor-free, fully printable mesoscopic perovskite solar cells as counter electrode. It was found that ultrathin graphite effectively increased the specific surface area of the carbon layer without sacrificing the conductivity. The large specific surface area facilitated the hole collection from the perovskite to carbon layer, correspondingly decreased the charge transfer resistance at the perovskite/carbon interface. Besides, the penetration of perovskite precursor solution in the carbon layer was accelerated due to the highly interconnected channels. As a result, the power conversion efficiency of the printable mesoscopic perovskite solar cell was significantly improved from 12.63% to 14.07% by incorporating ultrathin graphite instead of bulk graphite.

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## 1. Introduction

Organic-inorganic hybrid lead halide perovskite solar cells (PSCs) have become increasingly attractive in the field of photovoltaics due to their simple fabrication and high power conversion efficiency (PCE) [1–3]. Recently, the efficiency of PSC of 22.1% approaching the poly silicon solar cell has been certified by the National Renewable Energy Laboratory (NREL) [4], which indicates their great potential in photovoltaics markets. A typical PSC usually employs device architecture of TiO<sub>2</sub>/Perovskite/HTM/Au, in which the spiro-OMeTAD or PTAA are the most frequent choice of hole transport materials (HTM) [2,5,6]. However, the cost of spiro-OMeTAD or PTAA over ten times of the gold and the stability of such HTM under ambient air become a major concern for the development of PSCs [7]. Fortunately, besides the strong absorption coefficient, the typical perovskite materials such as MAPbI<sub>3</sub> appears high hole mobility, therefore it could be used as both of absorber and HTM material to achieve a simple and low-cost HTM-free PSCs [8].

Meanwhile, counter electrodes play a critical role in regulating heterojunction solar cells performance by collecting carriers [9,10].

The noble metal Au is the most efficient and thus widely used as counter electrode materials. But the expensive Au would increase manufacture cost of cells, which limits the industrialization progress. Therefore, much effort has been made to replace Au-based electrodes. In particular, the low-cost carbon materials possessing high electricity conductivity have become the most important candidate. In previous study, all sorts of carbon materials containing graphite, candle soot, CNT and mesoporous carbon were investigated. Y. Yang et al. applied flexible graphite sheet as carbon electrode in PSCs device, presenting a PCE of 10.2% [11]. Z. Wei et al. developed clamping perovskite solar cells using candle soot as hole extraction electrodes [12]. Z. Li et al. used laminated carbon nanotube networks as hole collection for perovskite solar cells and obtained a PCE of 6.29% [13]. Though the most studies focused on the planar carbon electrode based PSCs, the poor contact between perovskite and carbon electrode and the unmanageable thickness between the electron collecting layer and the carbon electrode will limit the repeatability and efficiency of the device.

To meet with the demand of low-cost, high efficient and repeatable photovoltaic device, a hole-conductor-free fully printable mesoscopic perovskite solar cells (MPSCs) have been developed in our group [14,15], which employs a triple layer of mesoporous TiO<sub>2</sub>, ZrO<sub>2</sub> and carbon as a scaffold and is infiltrated by the perovskite as a light harvester. The thickness between the electron collecting layer and the carbon electrode is accurately controlled by the ZrO<sub>2</sub> spacer layer. No hole conductor or Au

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reflector is employed [16–18]. Particularly, a new mixed-cation perovskite  $(5\text{-AVA})_x(\text{MA})_{1-x}\text{PbI}_3$  to replace  $\text{MAPbI}_3$  was applied in printable MPSCs and achieved a certified PCE of 12.84% with long stabilization in ambient air [14]. However, the used bulk graphite has a thick-layered structure with a small specific surface area. The larger surface area of the carbon layer brings the more highly interconnected channels, which is beneficial for the penetration of perovskite precursor solution. Therefore, it is worth developing the large surface area carbon layer without sacrificing the conductivity in PSC device.

In this work, we firstly utilized ultrathin graphite (UG) to replace bulk graphite (BG) to construct mesoporous conductive carbon films with a large specific surface area and then applied in MPSCs devices. Herein, the UG mixed with carbon black was used as counter electrode of the printable MPSC. In contrast with the bulk graphite/carbon black electrode (BGE), the ultrathin graphite/carbon black electrode (UGE) possessing a specific surface area of  $202.24\text{ m}^2\text{g}^{-1}$  exhibited a comparable square resistance at the same film thickness. The electrochemical impedance spectroscopy analysis of the UGE based device exhibited a lower charge resistance at the perovskite/carbon interface. Furthermore, the UGE had a better hole extraction ability and shorten the PL lifetime from 1.03 to 0.698 ns according to time-resolved photoluminescence measurement. Therefore, the MPSCs based on UGE achieved a high FF of 0.68 and thereby a higher efficiency of 14.07%.

## 2. Experimental

### 2.1. Fabrication of carbon paste

The UG was prepared by exfoliation of bulk graphite using wet ball milling as reported literature [19]. The carbon pastes were prepared by the following procedure as reported by us previously [20]. In brief, the BGs and UGs were mixed with carbon black in terpeneol solution, respectively. The hydroxypropyl cellulose was then added into the solution, followed by stirring vigorously via ball milling for 10 h.

### 2.2. Device fabrication

The fully printable MPSCs were prepared as reported [14]. The laser-patterned F-doped  $\text{SnO}_2$  (FTO) glass was ultrasonically cleaned with detergent, deionized water and ethanol successively. A  $\text{TiO}_2$  compact layer was then deposited on FTO substrate by spray pyrolysis at  $450\text{ }^\circ\text{C}$  with diisopropoxide bis(acetylacetonate) solution and sintered for 30 min. A mesoporous  $\text{TiO}_2$  layer was screen-printed on the compact layer and sintered at  $500\text{ }^\circ\text{C}$  for 40 min. Subsequently, a mesoporous  $\text{ZrO}_2$  space layer was deposited on the top of mesoporous  $\text{TiO}_2$  layer by screen-printing and sintered at  $500\text{ }^\circ\text{C}$  for 40 min. After cooling to room temperature, a mesoporous carbon layer was printed on the  $\text{ZrO}_2$  space layer and sintered at  $400\text{ }^\circ\text{C}$  for 30 min. Finally, a  $4\text{ }\mu\text{L}$   $(5\text{-AVA})_x(\text{MA})_{1-x}\text{PbI}_3$  perovskite precursor solution was dipped on the top of the carbon electrode. The device was accomplished after drying at  $50\text{ }^\circ\text{C}$  for 1 h.

### 2.3. Characterization

The morphology of samples was observed by a field-emission scanning electron microscope (SEM) (FEI Nova NanoSEM450) and transmission electron microscopy (TEM) (FEI Tecnai G2 20). The surface topography of UGs was analyzed by atomic force microscope (AFM) (Veeco Multimode) in the tapping mode. The Raman spectra of the BG and UG were obtained by Horiba Jobin Yvon LabRAM HR800 Raman system with the  $532\text{ nm}$  wavelength of a

$50\text{ mW}$  Nd-YAG laser at room temperature. The Brunauer–Emmett–Teller (BET) of samples was characterized by an Accelerated Surface Area and Porosimetry System (ASAP) 2020. The electrical conductivity of carbon films was obtained by a KDY-1 four point probe analyzer. The film thickness was measured by using profilometer (Dektak XT, Bruker). The wetting property of films was performed on a KinoSL200B contact angle goniometer. The photocurrent density-voltage characteristics were recorded by a Keithley 2400 sourcemeter under the air mass 1.5 (AM1.5) illumination at  $100\text{ mWcm}^{-2}$  using an Oriel 91192 solar simulator (Newport, USA). Electrochemical impedance spectroscopy (EIS) of the devices was performed on ZAHNER ENNIUM electrochemical workstations in the frequency range from  $100\text{ MHz}$  to  $4\text{ MHz}$ . The steady-state photoluminescence (PL) spectra were measured by a Horiba Jobin Yvon LabRAM HR800s with a  $532\text{ nm}$  wavelength excitation source. The time-resolved photoluminescence (TRPL) was measured at  $760\text{ nm}$  using excitation with a  $478\text{ nm}$  light pulse from Delta Flex Fluorescence Lifetime System (Horiba Scientific Com., Japan). The scatterer (Ludox suspension) was used as the instrument response function for deconvolution of the spectral value.

## 3. Results and discussion

The SEM image shown in Fig. 1 presents the morphology of UG and BG, respectively. The ultrathin graphite sheets tend to stick together to form fluffy agglomerate as shown in Fig. 1a. A magnified image of the agglomerates is shown in Fig. 1b, it can be clearly seen that UG has a diameter ranging from  $5$  to  $15\text{ }\mu\text{m}$  with coadjacent ultrathin graphite sheets, the size of which is similar to the BG (Fig. 1c–d). It is noted that edges of ultrathin graphite sheets are folded, indicating a small thickness. Fig. S1a displays the TEM image of partial ultrathin graphite sheets. Obviously, UGs have a highly transparent appearance with few-layer graphene, like transparent silk. To further investigate the thickness of UG, the AFM analysis in Fig. S1b is carried out. The vertical distance between the silicon substrate and the UG surface is regarded as the thickness of UG. From the height profiles (inset, Fig. S1b), it can be seen that the thickness of UG is approximately  $2\text{ nm}$ , which is estimated to be less than 10 layers of graphene [21]. Fig. S2 presents Raman spectra of the UG and BG. In general, the first-order Raman spectra of graphite materials present two intense feature bands. The G band at  $\sim 1580\text{ cm}^{-1}$  is corresponding to the  $E_{2g}$  phonon of  $\text{sp}^2$  carbon atoms and the D band at  $\sim 1350\text{ cm}^{-1}$  reflects the amount of disorder (compared to G band). In addition, the overtone of the D band, 2D band, is located at  $\sim 2700\text{ cm}^{-1}$ . The 2D peak at  $2693\text{ cm}^{-1}$  of UG is about  $21\text{ cm}^{-1}$  lower than that of the bulk graphite, which is consistent with the reported data of few-layer graphene [22]. In addition, the D/G peak intensity ratio of UG is about 0.13, much smaller than the value of graphene synthesized from the chemical reduction of graphene oxide [23], indicating UGs prepared by mechanical exfoliation method possibly have less structure defect and improved electrical conductivity. Fig. S3 shows low and high magnification images for the surface morphology of carbon electrodes based on UG and BG after sintering at  $400\text{ }^\circ\text{C}$ , respectively. Obviously, the surface of UGE is relatively rough (Fig. S3a) with massive ultrathin graphite vertically standing the film (Fig. S3b), which is beneficial for building conductive network structure.

Fig. 2a shows the  $\text{N}_2$  absorption and desorption curves of the carbon electrode (CE) based on BG and UG. Calculated by BJH (Barrett–Joyner–Halenda) method, the specific surface area value of UGE and BGE is  $202.24$  and  $69.01\text{ m}^2\text{g}^{-1}$ , respectively. The large specific surface area of the UGE provides more effective contact between the perovskite and carbon film. Therefore, the increase of specific surface area for the UGE contributes to hole collection from

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