Supplementary Materials for

A hole-conductor–free, fully printable mesoscopic perovskite solar cell with high stability

Anyi Mei, Xiong Li, Linfeng Liu, Zhiliang Ku, Tongfa Liu, Yaoguang Rong, Mi Xu Min Hu, Jiangzhao Chen, Ying Yang, Michael Grätzel, Hongwei Han*

*Corresponding author. E-mail: hongwei.han@mail.hust.edu.cn

Published 18 July 2014, Science 345, 295 (2014)
DOI: 10.1126/science.1254763

This PDF file includes:

Materials and Methods
Supplementary Text
Figs. S1 to S9
References
Materials and Methods

Materials synthesis

CH$_3$NH$_3$I (MAI) and HOOC(CH$_2$)$_4$NH$_3$I (5-AVAI) were synthesized as follows: Hydroiodic acid together with methylamine or 5-aminopentanoic acid were added with a mole ratio of 1:1 into round-bottom flask and stirred in the ice bath for 2h. After that the remaining liquid was evaporated in a rotavapor at 50 °C. The precipitate was washed three times with diethyl ether and dried in a vacuum drying oven.

The fabrication of perovskite based mesoscopic solar cells

As presented in Figure 1a, the FTO glass was first etched to form two separated electrodes before being cleaned ultrasonically with ethanol. Then, the patterned substrates were coated by a compact TiO$_2$ layer by aerosol spray pyrolysis, and a 1µm nanoporous TiO$_2$ layer was deposited by screen-printing of a TiO$_2$ slurry, which prepared as reported previously. After being sintered at 450 ºC for 30min, a 2µm ZrO$_2$ space layer was printed on the top of the nanoporous TiO$_2$ layer using a ZrO$_2$ slurry, which acts as an insulating layer to prevent electrons from reaching the back contact. Finally, a carbon black/graphite counter electrode with the thickness of about 10µm was coated on the top of ZrO$_2$ layer by printing carbon black/graphite composite slurry and sintering at 400 ºC for 30 min. After cooling down to room temperature, a 40wt% perovskite precursor solution was infiltrated by drop casting via the top of the carbon counter electrode. After drying at 50 ºC for one hour, the mesoscopic solar cells containing perovskite was obtained. The 40wt% perovskite precursor solution was prepared as follows: for the MAPbI$_3$ precursor solution, 0.395g MAI and 1.146g PbI$_2$ were dissolved in 2ml γ-butyrolactone and then stirred at 60 ºC overnight. The (5-AVA)$_x$(MA)$_{1-x}$PbI$_3$ precursor solution was prepared in the same manner except that a mixture of 5-AVAII and MAI with the mole ratio of 1:20 to 1:30 was used.

Characterization

In order to simulate the real condition of the perovskite in a working device, the 40wt% perovskite precursor solution was infiltrated by drop casting into a ZrO$_2$/TiO$_2$ double layer supported on the FTO glass substrate and then dried at 50 ºC. The X-ray diffraction (XRD) measurements employed a X’pert PRO X-ray Diffractometer and detected through the top of perovskite deposited ZrO$_2$/TiO$_2$/FTO glass substrate. The morphologies of perovskites on the nanoparticles were characterized by Tecnai GF30 transmission electron microscope (TEM) using particles scraped from the mesoporous TiO$_2$ films infiltrated with perovskites. Cross sectional SEM pictures of the devices and images from the top of the surface of mesoporous ZrO$_2$/TiO$_2$ films infiltrated with perovskites were obtained by a field-emission scanning electron microscope (FE-SEM). Photocurrent density voltage ($J-V$) curves were characterized with a Keithley 2400 source/meter and a Newport solar simulator (model 91192) giving light with AM 1.5G spectral distribution. A black mask with a circular aperture (0.07 cm$^2$) smaller than the active area of the square solar cell (0.5 cm$^2$) was applied on top of the cell. The incident photon conversion
efficiency (IPCE) was measured using a 150 W xenon lamp (Oriel) fitted with a monochromator (Cornerstone 74004) as a monochromatic light source. Time-resolved photoluminescence (PL) decay transients were measured at 760nm using excitation with a 482nm light pulse at a frequency of 4MHz from the Horiba Jobin Yvon Fluoromax-4 fluorimeter. These experiments employed TiO$_2$ and ZrO$_2$ mesoporous films filled with the respective perovskite. The UV-vis spectra were measured with the perovskite infiltrated mesoscopic TiO$_2$ films supported by FTO glass using a PerkinElmer Lambda 950 spectrophotometer.
Supplementary Text

XRD pattern

The XRD peak positions for MAPbI₃ agree with the known patterns for the MAPbI₃ tetragonal perovskite structure (S1). The strong reflections at 11.4, 14.1, 20, 28.3, 40.3 and 43.0 degree originate from lattice planes oriented in the (110), (220), (310), (322), (314) and (224) directions, respectively. The (110) and (220) reflections appear also for (5-AVA)ₓ(MA)₁₋ₓPbI₃ apart from several additional reflections at 5.8, 17.4, 23.2 and 33.9 degrees. These arise from (001), (002), (111) and (221) lattice planes, respectively, intercepting the C axis. (S2, S3)

This pattern fits an orthorhombic perovskite structure with the lattice parameters of a = 8.75 Å, b = 9.83 Å and c = 15.33 Å as compared to a = 8.49 Å, b = 8.49 Å and c = 12.64 Å for the tetragonal phase of MAPbI₃. It appears that and even at low 5-AVA/MA molar ratios, 5-AVA increases substantially the b and c lattice parameter.

A XRD spectrum was also taken from the blank ZrO₂/TiO₂/glass substrate (black curve in Fig. 2A). There is some overlap between these reflections and the diffraction peaks from the (220), (310) and (322) oriented lattice planes for (5-AVA)x(MA)₁₋ₓPbI₃ (blue curve) and the (221) and (201) oriented faces of MAPbI₃ (red curve). However this does not affect the principal conclusions of the above XRD analysis.

Perovskite Infiltration

In the absence of 5-AVA the crystals of perovskite precipitate and grow in a random fashion, forming nanoparticles in the pores and larger islands on the surface. Such islands are prone to block the access to the pores preventing further infiltration of the mesoporous oxide by perovskite. The pore filling is here incomplete and there is less intimate contact between the perovskite nanocrystals. The inhomogeneous nature of the loading of the TiO₂/ZrO₂ scaffold with neat MAPbI₃ becomes apparent from the mere inspection of the devices. The photos shown Figure S2 reveal a spotty coloration of the films, the darker and lighter regions indicating the presence and absence of filled and empty pores respectively or of perovskite islands forming a capping layer. By contrast the 5-AVA containing perovskite films crystals present uniform and deeper coloration affording improved solar light harvesting. By increasing the brightness and decreasing the contrast of the initial photographs, the difference in the homogeneity and depth of coloration can clearly be discerned.

UV-vis spectra

Thin films of MAPbI₃ perovskite have a dark reddish-brown color in transmission. This arises from the fact that their reciprocal absorption length in the 600-800 nm region is lower i.e. about 2~4 x10⁴ cm⁻¹ as compared to over 10⁵ cm⁻¹ at wavelength below 550 nm. Thicker films or films using a gold or silver back contact have a black appearance due to the increased optical path by light back reflection from the metal. Figure S3 compares the absorption spectra of films layer of mesoscopic TiO₂ infiltrated with MAPbI₃ or (5-AVA)x(MA)₁₋ₓPbI₃ obtained with a PerkinElmer Lambda 950 spectrophotometer. The (5-AVA)x(MA)₁₋ₓPbI₃ loaded film shows clearly a stronger
absorption in the red region compared to MAPbI₃. In particular, for (5-AVA)$_x$(MA)$_{1-x}$PbI₃ the ratio of the absorbance in the 600-750nm range over that at 500 nm is much larger than for MAPbI₃. This indicates that the optical cross section of (5-AVA)$_x$(MA)$_{1-x}$PbI₃ at longer wavelengths near the band gap is larger than for MAPbI₃.
**Fig. S1.** Time-resolved PL measurements taken at the peak emission wavelength of the MAPbI$_3$ and (5-AVA)$_x$(MA)$_{1-x}$PbI$_3$ perovskites deposited into the mesoporous scaffolds of ZrO$_2$ or TiO$_2$.

**Fig. S2.** Photographs of (A) (5-AVA)$_x$(MA)$_{1-x}$PbI$_3$ and (B) MAPbI$_3$ based mesoscopic solar cells. Inset: enhanced images through increasing the brightness and decreasing the contrast of the initial photographs.
**Fig. S3.** The UV-vis spectra of FTO glass/TiO₂ films filling with (5-AVA)ₓMA₁₋ₓPbI₃ and MAPbI₃.

**Fig. S4.** Stability test of a triple layer (5-AVA)ₓ(MA)₁₋ₓPbI₃ perovskite sensitized mesoscopic solar cell effected in full AM 1.5 simulated sunlight in ambient air over 1008 hours with an unsealed device, the perovskite being protected by the carbon layer acting as back contact.
**Fig. S5.** $J$-$V$ curves of triple layer perovskite $(5$-AVA)$_x$(MA)$_{(1-x)}$PbI$_3$ sensitized solar cells at different scanning directions: forward bias scan from 0V to $V_{oc}$ and back to 0V. The scanning rate was 3 mV s$^{-1}$.
Fig. S6. Independent certificate by Newport Corporation, an accredited PV laboratory confirming a power conversion efficiency of 12.84% with photocurrent density of 22.8 mA cm$^{-2}$ for our triple layer hole conductor-free mixed 5-AVA-MA perovskite solar cell.
Fig. S7. $J-V$ curve of a printed mesoscopic perovskite solar cell without ZrO$_2$ layer.

Fig. S8. Photovoltaic characteristics of 20 randomly selected (5-AVA)$_x$(MA)$_{1-x}$PbI$_3$ based mesoscopic solar cells fully printed on a 10cm×10cm FTO glass.
Fig. S9. An array of mesoscopic solar cells array printed on 10cm×10cm FTO glass.
REFERENCES