Perovskite Solar Cells



# Design of an Inorganic Mesoporous Hole-Transporting Layer for Highly Efficient and Stable Inverted Perovskite Solar Cells

Yu Chen, Zhou Yang, Shubo Wang, Xiaojia Zheng, Yihui Wu,\* Ningyi Yuan,\* Wen-Hua Zhang,\* and Shengzhong (Frank) Liu

The unstable feature of the widely employed organic hole-transporting materials (HTMs) (e.g., spiro-MeOTAD) significantly limits the practical application of perovskite solar cells (PSCs). Therefore, it is desirable to design new structured PSCs with stable HTMs presenting excellent carrier extraction and transfer properties. This work demonstrates a new inverted PSC configuration. The new PSC has a graded band alignment and bilayered inorganic HTMs (i.e., compact NiO<sub>x</sub> and mesoporous CuGaO<sub>2</sub>). In comparison with planar-structured PSCs, the mesoporous CuGaO2 can effectively extract holes from perovskite due to the increased contact area of the perovskite/HTM. The graded energy alignment constructed in the ultrathin compact NiOx, mesoporous CuGaO<sub>2</sub>, and perovskite can facilitate carrier transfer and depress charge recombination. As a result, the champion device based on the newly designed mesoscopic PSCs yields a stabilized efficiency of ~20%, which is considered one of the best results for inverted PSCs with inorganic HTMs. Additionally, the unencapsulated PSC device retains more than 80% of its original efficiency when subjected to thermal aging at 85 °C for 1000 h in a nitrogen atmosphere, thus demonstrating superior thermal stability of the device. This study may pave a new avenue to rational design of highly efficient and stable PSCs.

Organic–inorganic lead-halide-based perovskite solar cells (PSCs) have drawn tremendous attention due to their remarkable optoelectronic properties.<sup>[1]</sup> The certified power conversion efficiencies (PCEs) have exceeded 22% over a few years by designing the device architecture, tailoring the formation, and

Y. Chen, Dr. X. Zheng, Dr. Y. Wu, Prof. W.-H. Zhang Sichuan Research Center of New Materials Institute of Chemical Materials China Academy of Engineering Physics 596 Yinhe Road, Shuangliu, Chengdu 610200, China E-mail: yihuiwu@caep.cn; whzhang@caep.cn Y. Chen, S. Wang, Dr. Y. Wu, Dr. N. Yuan Jiangsu Province Cultivation Base for State Key Laboratory of Photovoltaic Science and Technology Changzhou University Changzhou, Jiangsu 213164, China E-mail: nyyuan@cczu.edu.cn Prof. Z. Yang, Prof. S. F. Liu School of Materials Science and Engineering Shanxi Normal University

Xi'an 710119, China

D The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.201805660.

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composition of the light harvester,<sup>[2]</sup> which is now on par with that of the traditional photovoltaic devices, such as Cu(In,Ga) Se<sub>2</sub>, CdTe, and multicrystalline silicon solar cells. As of now, the hole-transporting materials (HTMs) used for state-of-theart PSC devices are either spiro-MeOTAD (2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl) amino]-9,9'-spirobifluorene) or PTAA (poly[bis(4-phenyl)(2,4,6-trimethylphenyl) amine]).<sup>[3]</sup> Traditionally, additives such as lithium salts (Li-TFSI), cobalt complexes, and 4-tert-butyl pyridine (TBP) are needed to attain good conductivity for both HTMs to achieve high device efficiency. Unfortunately, spiro-OMeTAD will degrade nonreversibly owing to the evaporation of the dopants when the temperature is over 90 °C, which will further lead to severe degradation of PSCs.<sup>[4]</sup> Another important degradation pathway has been identified as the degradation of organic charge transporting layers, the interfaces, and device structure.<sup>[5]</sup> These disadvantages have

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become the main obstacles in achieving long-term operational and highly thermal stable PSCs. Therefore, it is highly desirable to develop suitable alternative HTM that offer satisfactory performance with long-term thermal stability.

It is well known that, in comparison with the widely used organic HTMs, inorganic materials show significantly better stability, and many materials, such as CuSCN,<sup>[6]</sup> CuI,<sup>[7]</sup> CuO<sub>x</sub>,<sup>[8]</sup> NiO<sub>x</sub>,<sup>[9]</sup> MoO<sub>3</sub>,<sup>[10]</sup> CuGaO<sub>2</sub>,<sup>[11]</sup> and CuCrO<sub>2</sub>,<sup>[12]</sup> have been explored as HTMs in both normal structured and inverted configuration PSCs. However, most of the PSCs with inorganic HTMs exhibit relatively inferior performance to their counterparts with organic HTMs. The main reason for the inferior performance is that very few inorganic HTMs can simultaneously present features of high hole mobility, good thermal stability, and a well-matched work function. These features are necessary to achieve good device performance for PSCs. CuGaO<sub>2</sub> possesses many potential advantages for being used as an HTM in PSCs because of its large bandgap ( $\approx$ 3.6 eV), high hole mobility (10<sup>-2</sup> to 10<sup>1</sup> cm<sup>2</sup> · V<sup>-1</sup> s<sup>-1</sup>), and low-lying valence band maximum (VBM) (≈5.3 eV).<sup>[13]</sup> PSC with an encouraging PCE of 18.5% and good stability has recently been obtained when CuGaO<sub>2</sub> was used as an HTM in a normal planar-structured device, thus revealing its application potential in PSCs.<sup>[11]</sup>



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Figure 1. a) XRD patterns of the as-synthesized CuGaO<sub>2</sub>. b) TEM image and c) HRTEM image of the CuGaO<sub>2</sub> NPs (inset: corresponding FFT pattern). d) Surface SEM image of the mesoporous CuGaO<sub>2</sub> film.

Overall, mesoscopic-structured PSCs with mesoporous TiO<sub>2</sub> building blocks usually exhibit higher device efficiency than their planar counterparts. The higher device efficiency is due to better charge extraction, which benefits from an enlarged charge separation area at the perovskite/TiO2 interface.<sup>[1g,2,3,6a,14]</sup> Recently, PSCs based on mesoporous SnO<sub>2</sub> has been developed by Fang and co-workers and excellent results were achieved compared to the planar device, demonstrating the superiority of the mesoscopic structure.<sup>[15]</sup> This inspired us to design a new PSC configuration with mesoporous inorganic hole-transporting layer for devices with both high efficiency and high stability. Herein, we designed an inverted mesoscopic PSC with mesoporous HTMs, in which an ultrathin NiO<sub>x</sub> (<10 nm) was introduced as the compact layer, and mesoporous CuGaO2 was then deposited on it to form a bilayered, graded band alignment inorganic HTM. The graded energy alignment of the VBM between NiO<sub>v</sub>, CuGaO<sub>2</sub>, and perovskite is very favorable for charge carriers transfer and collection. As a result, the device based on the new structure yielded a steady output efficiency of  $\approx 20\%$  and showed significantly improved long-term thermal stability. The new structure demonstrates superiority in achieving highly efficient and stable PSCs.

**Figure 1**a shows X-ray diffraction (XRD) patterns of the as-synthesized CuGaO<sub>2</sub> nanocrystals (NCs). All diffraction peaks can be indexed to rhombohedral-structured CuGaO<sub>2</sub> (JCPDS No. 41-0255), confirming the high purity of the NCs.



The morphology of the NCs was confirmed to be the hexagonal plates by transmission electron microscopy (TEM) as shown in Figure 1b. The sample displays a narrow distribution with an average size of 55 nm and a thickness of ≈12 nm (Figure S1, Supporting Information). The high-resolution transmission electron microscopy (HRTEM) image (Figure 1c) indicates that CuGaO<sub>2</sub> nanoplates (NPs) are highly crystalline with continuous lattice fringes across the NP. The corresponding fast Fourier transform (FFT) pattern on a single NP confirms the single crystalline nature. Additionally, the interplanar crystal spacing of 0.148 nm matches well with d<sub>110</sub> of rhombohedral-structured CuGaO<sub>2</sub>, indicating that the exposed crystal facet is (001), which agrees with the XRD results. The elemental composition of the asprepared CuGaO<sub>2</sub> NPs was analyzed by X-ray photoelectron spectroscopy (XPS), as shown in Figure S2 in the Supporting Information. The Cu  $2p_{3/2}$  and Ga  $2p_{3/2}$  peaks were identified at 932.3 and 1117.6 eV, corresponding to Cu<sup>+</sup> and Ga<sup>3+</sup>, respectively. The O 1s peak located at 530.4 eV can be attributed to the lattice oxygen O2- in crystal lattice while the additional peak at 531.8 eV should be derived from the chemisorbed oxygen species at the oxygen vacancies.<sup>[16]</sup> Elemental mapping (Figure S3, Supporting Information) also disclosed the homogenous distribution of the

elements contained. Therefore, we have achieved the CuGaO<sub>2</sub> NPs with narrow size distribution and high crystallinity.

Mesoporous CuGaO<sub>2</sub> film (Figure 1d) was fabricated on the NiO<sub>x</sub> compact layer by spin-coating a paste containing CuGaO<sub>2</sub> NPs, terpineol, ethylcellulose, and isopropyl alcohol, and was subjected to annealing at 350 °C for 30 min. The energy levels of the CuGaO<sub>2</sub> film were studied by ultraviolet photoelectron spectroscopy (UPS) and UV-vis spectroscopy, as shown in Figure S4 in the Supporting Information. The VBM of CuGaO<sub>2</sub> was determined to be -5.32 eV relative to vacuum level; this result is consistent with previous reports.<sup>[11,17]</sup> The conduction band minimum (CBM) of CuGaO2 was deduced to be -1.68 eV, which is above the CBM of the perovskite film. The compatible energy levels make it efficient to extract the photoinduced holes from the perovskite into the CuGaO2 and to block electrons from injecting into the CuGaO2. The existence of the ultrathin NiO<sub>x</sub> (<10 nm) underlying the CuGaO<sub>2</sub> mesoporous film, working as the compact layer, can avoid the direct contact between fluorine-doped tin oxide (FTO) and the perovskite in consideration of the mesoporous nature of the CuGaO<sub>2</sub> film. Additionally, the graded energy alignment of the VBMs between NiO<sub>x</sub>, CuGaO<sub>2</sub>, and perovskite, as shown in Figure 2b, is beneficial for carrier transfer and collection, which is prerequisite to achieving excellent device performance.<sup>[18]</sup>

To testify the efficacy of such brand-new mesoporous inorganic-HTM-based PSCs, a control device with a planar structure, i.e., with planar  $CuGaO_2$  film as an HTM, was







**Figure 2.** a) Schematic illustration of the device configuration and a typical cross-sectional SEM image for the champion device. b) Energy-level diagram exhibiting the collection process of photoinduced holes. c) J-V curves of the devices based on planar and mp CuGaO<sub>2</sub> HTM. d) IPCE curves and the corresponding integrated photocurrent for devices based on planar and mp CuGaO<sub>2</sub> HTM. e) The steady output efficiency of the champion device based on mp CuGaO<sub>2</sub> HTM around the maximum output power point a function of time under simulated 1 sun illumination.

fabricated. Figure S5 in the Supporting Information shows the surface scanning electron microscopy (SEM) images of perovskite films formed on mesoporous (mp) CuGaO<sub>2</sub> and on planar CuGaO<sub>2</sub>. Both films show full surface coverage and dense film morphology with crystal grains in the range of 150-350 nm, indicating that the formation of mesopores within CuGaO2 does not significantly affect the crystallization of the perovskite film in comparison with the planar film. The root mean square (RMS) roughness of the perovskite films were both identified to be ≈11 nm by atomic force microscopy (AFM), as shown in Figure S6 in the Supporting Information. To achieve the ideal PSC performance, we have made two-step optimization of the CuGaO<sub>2</sub>-perovskite system: At first, the thickness of mp CuGaO<sub>2</sub> was studied while the process parameters of perovskite film was fixed. It was found that the thickness of CuGaO<sub>2</sub> films (ranging from 70 to 260 nm) posed an important influence on the thicknesses of perovskite films (as shown in Figure S7b-e in the Supporting Information). The comparison was presented in Figure S7a in the Supporting Information for the PCEs of the resulting PSCs with different thickness of mp CuGaO<sub>2</sub> as HTM. A volcanic curve was formed. The average PCEs of the present PSCs varied from 17.5% to 19.5% and peaked for the device with an mp CuGaO<sub>2</sub> thickness of  $\approx$ 130 nm. We then systematically investigated the fabrication processing parameters for perovskite film, including spin speed, annealing temperature, the precursor concentration and so on. A typical crosssectional SEM image for the best mesoscopic device (shown in Figure 2a) shows that the thickness of each layer is 8, 130, 600, 60, and 80 nm for compact NiO<sub>x</sub>, mp CuGaO<sub>2</sub>, perovskite, PC<sub>61</sub>BM and BCP, and Ag, respectively. To reveal the role of the present mesoporous HTM, a planar PSC with a planar CuGaO<sub>2</sub> layer with similar thickness was also prepared for comparison. Figure 2c and Figure S8 in the Supporting Information

present the *J*–*V* characteristics of the best devices with planar and *mp* CuGaO<sub>2</sub> as HTMs under standard AM 1.5 illumination (at 100 mW cm<sup>-2</sup>). The main photovoltaic parameters, including short-circuit current density (*J*<sub>SC</sub>), open-circuit voltage (*V*<sub>OC</sub>), fill factor (FF), and PCE, are summarized in **Table 1**. The control champion planar device exhibits a PCE of 17.37% with *J*<sub>SC</sub> = 22.17 mA cm<sup>-2</sup>, *V*<sub>OC</sub> = 1080 mV, and FF = 72.48%, whereas the PCE for the champion device with *mp* CuGaO<sub>2</sub> HTM is jumped to 20.13% with *J*<sub>SC</sub> = 22.23 mA cm<sup>-2</sup>, *V*<sub>OC</sub> = 1132 mV, and FF = 79.96%. The improvement of the device efficiency is mainly attributed to the significantly enhanced *V*<sub>OC</sub> and FF for the inverted *mp*-CuGaO<sub>2</sub>-based device.

As a control, PSC devices with only either NiO<sub>x</sub> film or mp CuGaO<sub>2</sub> film as HTM were studied. The corresponding device parameters are provided in Figure S9 and Table S1 in the Supporting Information. PCEs of 15.93% and 16.41% were obtained for NiO<sub>x</sub>-only and mp CuGaO<sub>2</sub>-only cells, respectively. Both are significantly inferior to the device with the combination of the mesoporous CuGaO<sub>2</sub>/NiO<sub>x</sub> HTMs. It is worth noting that the V<sub>OC</sub> of the devices are lower than the previously reported results based on NiO and PTAA.<sup>[9a,19]</sup> The lower V<sub>OC</sub> for the NiO<sub>x</sub>-only device (1051 mV) could be attributed to the

 $\ensuremath{\text{Table 1.}}$  The key photovoltaic parameters of the PSCs with different structure.

	Scan direction	V <sub>OC</sub> [mV]	J <sub>sc</sub> [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]	Stabilized PCE [%]
Planar CuGaO <sub>2</sub>	Re	1081	22.17	72.48	17.37	16.72
	Fw	1046	22.20	57.06	13.25	
<i>mp</i> CuGaO <sub>2</sub>	Re	1132	22.23	79.96	20.13	19.95
	Fw	1093	21.88	73.68	17.62	



ultrathin thickness of our NiOx film (with thickness of only  $\approx$ 8 nm) and the relatively lower crystallinity of NiO<sub>x</sub> (due to the low temperature processing). The lower  $V_{OC}$  for mp CuGaO<sub>2</sub>only device (1023 mV) should be ascribed to the absence of compact layer, which may induce partial contact of FTO and perovskite. To further confirm the importance of the hole compact layer, PTAA was used as the hole-transporting layer (HTL). As shown in Figure S9 and Table S1 in the Supporting Information, 1088 mV of the  $V_{\rm OC}$  was obtained, approaching the results reported by Zhu and co-workers ( $V_{OC} = 1100$  mV for the device without secondary growth of the perovskite).<sup>[19c]</sup> When the NiO<sub>x</sub> and mp CuGaO<sub>2</sub> were combinatively used as the bilayer HTL, the  $V_{\rm OC}$  of our champion device is boosted to 1132 mV, which is on par with the results based on PTAA reported by Huang and co-workers ( $V_{OC} = 1140 \text{ mV}$ ).<sup>[3d]</sup> Therefore, the synergistic role of the compact NiO<sub>x</sub> and mp CuGaO<sub>2</sub> was critical in achieving efficient PSCs with high  $V_{\rm OC}$  in this study.

In order to further broaden the application scope of NiO<sub>x</sub>/mp CuGaO<sub>2</sub> HTL, wide-bandgap perovskite with Eg of 1.73 eV was employed as the light harvester. As shown in Figure S9 and Table S1 in the Supporting Information, 1181 mV of the  $V_{OC}$  can be obtained, which is higher than the results based on PTAA ( $V_{OC} = 1150$  mV for perovskite with Eg = 1.72 eV),<sup>[3d]</sup> and is close to the highest  $V_{OC}$  reported for wide-bandgap PSCs ( $V_{OC}$  is over 1220 mV, Eg = 1.74 eV).<sup>[3f]</sup> Nevertheless, there is still plenty of room to further push  $V_{OC}$  up to an even higher level after systematical optimization of the inverted widebandgap PSCs based on NiO<sub>x</sub>/mp CuGaO<sub>2</sub>.

Figure 2d shows the corresponding incident-photon-to-current conversion efficiency (IPCE) spectra for the two cells with both CuGaO<sub>2</sub> planar film and mesoporous film. The integrated photocurrent densities are 21.36 and 21.82 mA cm<sup>-2</sup> for devices with planar and *mp* CuGaO<sub>2</sub> HTM, respectively, which are

approximate to the  $J_{SC}$  values extracted from the corresponding *I–V* curves. Compared to the planar PSCs, the external quantum efficiency (EQE) value for the CuGaO<sub>2</sub> mesoscopic PSCs in the short wavelength range is almost the same while it is much higher in the long wavelength range beyond 550 nm. This phenomenon should be ascribed to the pronounced light scattering in the mp CuGaO<sub>2</sub> film, which further increased the light absorption in perovskite layer (Figure S10, Supporting Information). Similar results were obtained from the optical transmission spectra. As shown in Figure S11 in the Supporting Information, mp CuGaO<sub>2</sub> shows higher transparency than FTO and planar CuGaO<sub>2</sub> in the range of 500-800 nm, attributable to the light scattering and reduced reflection. The higher transparency of the CuGaO<sub>2</sub> mesoscopic films will increase the light absorption of the perovskite and produce a higher photocurrent. Specifically, higher *I*<sub>SC</sub> can be obtained in this case. Steady-state output efficiency measured at the maximum power point voltage  $(V_{mpp})$ was then studied to accurately assess the performance of the mesoscopic and the planar devices, as shown in Figure 2e and Figure S12 in the Supporting Information. The PCE of the mesoscopic device stabilizes at ≈19.95%, which is among the highest efficiency currently reported for inverted PSCs with inorganic HTMs.<sup>[12,19a,20]</sup> In contrast, the planar device presents a steady output efficiency of 16.72%. These results demonstrate the superiority of the NiO<sub>v</sub>/CuGaO<sub>2</sub> mesoporous structure in achieving high-efficiency PSC devices. To assess the reproducibility of our devices, 30 individual cells for the planar and mesoscopic devices were fabricated; the detailed parameters are shown in Figure 3. It is clear that all the key *I*–V parameters of the *mp* CuGaO<sub>2</sub>based PSCs are better, and the corresponding distributions are narrower in comparison with the planar devices. The results confirm the reliability of our method to fabricate high-efficiency inverted PSCs using graded NiO<sub>x</sub>/mesoporous CuGaO<sub>2</sub>



Figure 3. Statistics of the device based on planar and mp CuGaO<sub>2</sub> HTM: a)  $J_{SC}$ , b)  $V_{OC}$ , c) FF, and d) PCE.







**Figure 4.** Long-term stability of the planar and mesoscopic unsealed devices stored at dark under ambient conditions with humidity of 40–70%: a)  $J_{SC}$ , b)  $V_{OC}$ , c) FF, d) PCE, and e) thermal aging of both devices at 85 °C in a nitrogen atmosphere.

HTMs. Remarkably, it can also be seen that the improved performance is directly related to the enhanced  $V_{\rm OC}$  and FF. The enhancement of  $V_{\rm OC}$  should be related to the reduced interfacial defects.<sup>[18a]</sup> High FF (>75%) usually means the absence of large carrier extraction/injection barrier for the interface between perovskite and HTM/ETM.<sup>[21]</sup> The FF of the present mesoscopic devices is between 76% and 80%, indicating that the mesoscopic device structure and graded energy alignment can effectively improve carrier transfer and collection.

The stability of the device is a critical issue in determining the application potential for PSCs in the future. Therefore, the long-term stability of the PSC device was investigated. **Figure 4**a–d and Table S2 in the Supporting Information show the main parameters for the unencapsulated planar and mesoscopic devices. The PCE retains more than 90% of its initial efficiency after being stored for two months under ambient conditions for the mesoscopic one. Moreover, less than 20% of the efficiency loss can be observed even after 1000 h thermal aging at 85 °C (shown

in Figure 4e), demonstrating its superior thermal stability and high tolerance to humidity. The excellent thermal stability of the present mesoscopic PSCs could be attributed to two factors: 1) the (FA,Cs) double cations perovskite adopted in this work is a thermally stable perovskite system in comparison with the methylammonium (MA)-containing perovskites.<sup>[22]</sup> 2) More importantly, the inorganic NiO<sub>x</sub>/mesoporous CuGaO<sub>2</sub> are even more thermally stable than the (FA,Cs) double cations perovskite.

To understand the large enhancement of the photovoltaic (PV) performance,  $J_{SC}$  as a function of light intensity (0.1 sun  $\leq$  light intensity  $\leq$  1 sun) was measured and a linear correlation can be found, as shown in **Figure 5a**. The planar device gives a slope of 0.97, and the mesoscopic cell presents a slope of 0.98. Both data approach 1, indicative of no space-charge effect for both devices,<sup>[23]</sup> and confirming the negligible bimolecular recombination (a reverse process of light absorption) for both devices.<sup>[24]</sup> These results are in good agreement with recently reported results that the bimolecular charge carrier







Figure 5. a)  $J_{SC}$  and b)  $V_{OC}$  versus light intensity for the devices based on the planar and mp CuGaO<sub>2</sub> HTM. c) Steady PL spectra of perovskites and d) TRPL decay profiles of the perovskites fabricated with different HTMs.

recombination in perovskite film is negligible at low light intensity, and it begins to dominate only when the light intensitv is around 100 suns.<sup>[25]</sup> The predominant species in perovskites are free charge carrier rather than excitons due to that the exciton binding energy for perovskites at room temperature is quite low. Therefore, trap-assisted monomolecular recombination of electrons or holes is the main recombination process in a PSC.<sup>[26]</sup> We then studied the relationship between  $V_{OC}$  and light intensity (as shown in Figure 5b). The slope was decreased from 1.51 kT  $q^{-1}$  for the planar cell to 1.38 kT  $q^{-1}$  for the mesoscopic device, meaning that the trap-assisted recombination is significantly reduced due to the well-improved interface resulting from CuGaO<sub>2</sub> mesoporous structure and the graded energy alignment.<sup>[27]</sup> The space-charge limited current (SCLC) method was further employed to examine the defect states in the perovskite layer. Figure S13 in the Supporting Information shows the corresponding current-voltage (I-V) curves measured from a hole-injecting device. Three distinct regions can be identified in the I-V curve: an Ohmic region with the order n = 1, a Child region with n = 2, and a trap-filling limited (TFL) region with n > 3. The voltage marking the transition from the Ohmic region to the TFL region, V<sub>TFL</sub>, is used to calculate the trap-state densities close to the VBM.<sup>[28]</sup> According to Equation (1):

$$V_{\rm TFL} = \frac{e n_{\rm t} L^2}{2\varepsilon \varepsilon_0} \tag{1}$$

where *e* is the elementary charge,  $n_{\rm t}$  is the trap density, *L* is the thickness of the crystal between two Au electrodes,  $\varepsilon$  is

the relative dielectric constant of FAPbI<sub>3</sub> ( $\varepsilon = 46.9$ ),<sup>[29]</sup> and  $\varepsilon_0$ is the dielectric constant of vacuum. The  $V_{\rm TFL}$  of the devices based on planar and mp CuGaO2 are 0.12 and 0.07 V, respectively. Therefore, the hole trap state density was reduced from  $1.14 \times 10^{15}$  cm<sup>-3</sup> for the pristine ones to  $6.54 \times 10^{14}$  cm<sup>-3</sup> for the mesoscopic device, which agrees well with the conclusion from Figure 5b that the mesoscopic device results in a reduced trap recombination. Additionally, from the Child region in Figure S13 in the Supporting Information, the carrier mobility can be extracted by the Mott-Gurney law.<sup>[30]</sup> The hole mobility was calculated to be  $1.01 \times 10^{-2}$  and  $2.33 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively, for the planar and the mesoscopic structured perovskites, suggestive of the improved charge transfer. In short, the formation of the mesoscopic structure and graded energy alignment in the mesoporous-CuGaO2-based PSCs can reduce trap state density and suppress charge recombination, which is highly beneficial for obtaining excellent device performance.

The carrier kinetics of the planar and mesoscopic PSCs devices were then studied by the steady and time-resolved photoluminescence (PL) spectroscopies. Figure 5c shows that the pristine perovskite exhibits a strong steady PL peak near the edge of the bandgap, while the introduction of NiO<sub>x</sub> quenches the signal by 60%. Noticeably, the combination of the compact NiO<sub>x</sub> layer and the planar CuGaO<sub>2</sub> quenches the PL signal by 94%. This band edge PL signal was further quenched by over 96% when the compact NiO<sub>x</sub> and the *mp* CuGaO<sub>2</sub> was combinatively used as bilayered HTM. These results demonstrate that the formation of mesoscopic structure with graded energy alignment plays a positive role in facilitating the charge transfer from perovskite to the HTMs with less energy loss; thus,

superior hole-collection could be expected for the mesoscopic structured PSCs. Similar results were further provided by the time-resolved PL (TRPL) spectroscopy (shown in Figure 5d). The TRPL decay curves are fitted by the biexponential function (Equation (2)) and the fitted data are summarized in Table S3 in the Supporting Information.

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$$f(t) = A_1 \exp^{(-t/\tau_1)} + A_2 \exp^{(-t/\tau_2)} + B$$
(2)

where  $\tau_1$  is the fast transient component that corresponds to the surface property, and  $\tau_2$  is the slow component that comes from the bulk property. *B* is a constant for the baseline offset.  $A_1$  and  $A_2$  are the constants representing the contributions of the fast and slow components, respectively.<sup>[31]</sup> For the pristine perovskite, the PL decay times are  $\tau_1 = 2.41$  ns and  $\tau_2 = 432.9$  ns. For the sample with single NiO<sub>x</sub> as HTM, the slow decay lifetime ( $\tau_2$ ) was reduced to 298.7 ns. When the NiO<sub>x</sub> was combined with CuGaO<sub>2</sub> as bilayer HTM,  $\tau_2$  values were further decreased to 69.27 ns for the planar sample, and 23.62 ns for the mesoscopic one, respectively, indicating that the formation of the mesoscopic structure with graded energy alignment is more efficient in realizing carrier separation and transfer than the planar structure. The average PL decay lifetime can also be obtained via Equation (3):

$$\tau_{\text{ave}} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \tag{3}$$

The  $\tau_{\rm ave}$  for the pristine perovskite-only sample is 419.8 ns, indicative of its high quality film.<sup>[2,3d,19b]</sup> The average PL decay time of the perovskite is reduced to 284.2 ns upon introducing the NiO<sub>x</sub> compact layer. Moreover, PL decay times of the perovskite were further decreased to 49.97 and 16.56 ns, respectively, for the NiO<sub>x</sub>/planar CuGaO<sub>2</sub> film and NIO<sub>x</sub>/mp CuGaO<sub>2</sub> films, meaning that the holes transfer faster for the bilayered mesoscopic structure than the planar one. It is well known that the reduced PL decay time is beneficial for suppressing the charge recombination at the interface and for effectively improving device performance. We then performed electrochemical impedance spectroscopy (EIS) to study the interfacial carrier transfer and transport kinetics. Figure S14 in the Supporting Information shows the Nyquist plots of the devices based on planar and mp CuGaO<sub>2</sub>. The arcs at high frequency should be ascribed to carrier transport features in the bulk layer and the incomplete semicircles in the low frequency represent carrier recombination process at the interfaces.<sup>[27a,32]</sup> The corresponding values of  $R_s$  (internal series resistance),  $R_{tr}$  (transport resistance), and  $R_{\rm re}$  (recombination resistance) were fitted by Z-view software with the given equivalent circuit and summarized in Table S4 in the Supporting Information. The mesoscopic device displays a lower  $R_{tr}$  and higher  $R_{rec}$  compared to the planar one. This result indicates a faster carrier transfer and a lower recombination rate and is in agreement with the TRPL results. Therefore, the PV parameters for the mesoscopic-structured PSCs are significantly enhanced in comparison with the planar PSCs. The present brand-new structure can not only increase the contact area of perovskite/HTM and shorten the hole diffusion pathways in the perovskite layer, which favors the charge separation and interfacial trap state passivation. More importantly, the bilayered HTM structure results in the formation of graded energy alignment at the interface, leading to favorable band bending at the valence band edge for improved carrier transporting between each layer.<sup>[18b]</sup> All of these characteristics can effectively enhance carrier transfer and depress carrier recombination. As a result, high-efficiency PSCs can be obtained for the mesoscopic-structured PSCs in this study.

In summary, we have developed a strategy to improve both the efficiency and stability of inverted PSCs by designing a bilayer inorganic mesoporous HTM. The formation of mesoporous structure and well matched energy levels of the VBMs improve the charge carrier transfer and collection, reduce interfacial trap states. Additionally, the device made of the mesoscopic structure has achieved a stabilized PCE of  $\approx$ 20%, which is superior to that of the planar cell (16.72%). Moreover, the inorganic-HTM-based device exhibits excellent long-term thermal stability. Our findings indicate that the rational design of a suitable device configuration may be an effective method for attaining efficient and stable PSCs.

#### **Experimental Section**

Device Fabrication: Devices were prepared on cleaned and patterned FTO substrates. The dense NiOx was prepared via electron beam evaporation. And then 50 mg of CuGaO<sub>2</sub> powdered materials were mixed with 400  $\mu$ L isopropyl alcohol. This mixture was then ultrasonicated for 30 min and poured dropwise in 3.32 mL of Terpineol and 4 mL of isopropyl alcohol/ethylcellulose (9:1) to form the paste with a suitable viscosity, and then the paste was deposited on NiOx-coated FTO substrates (Pilkington TEC8, 14  $\Omega$  sq<sup>-1</sup>) by spin coating. This *mp* CuGaO<sub>2</sub> films can be obtained after annealing at 350 °C for 30 min to burn off the organic. For comparison, the planar CuGaO<sub>2</sub> film was prepared by directly spin coating the isopropyl alcohol suspension. The perovskite layer was deposited by using a green solvent-processed method in a nitrogen-filled glovebox. The precursor solution was comprised of 52 mg of CsI, 174 mg of FAI, 560 mg of PbI<sub>2</sub>, 50 mg of PbBr<sub>2</sub>, 17 mg of FABr in 1 mL of dimethyl formamide (DMF) and dimethylsulfoxide (DMSO) (4:1, v/v). The solution was spin-coated onto the CuGaO<sub>2</sub> substrates by a consecutive two-step spin-coating process at 1000 and 6000 rpm for 10 and 40 s, respectively. During the second spin-coating step, 120 µL Anisole was dropped onto the substrate after 20 s. And then the substrate was annealed at 100 °C for 20 min. An electron-transporting layer was coated with a solution of  $PC_{61}BM$  dissolved in anisole (20 mg mL<sup>-1</sup>) at 3000 rpm for 30 s and followed by a saturated BCP solution at 5000 rpm for 30 s. Finally, a 100 nm thick Ag electrode was deposited by thermal evaporation to complete the device fabrication.

Characterization: The XRD was measured on Maxima 7000 diffractometer (Shimadzu, Japan) with a Cu Ka radiation (40 kV, 100 mA). Energy levels of CuGaO2 were detected by Thermo escalab 250XI. The film morphology was obtained by using a Titachi S5200 field-emission SEM (Hitachi High Technologies Corporation). The UVvis spectra were measured using an Evolution 201 spectrophotometer (Thermo Fisher Scientific Corporation). The NP morphology, elemental mapping, and lattice spacing were examined by TEM (Carl Zeiss SMT Pte, Ltd Libra 200FE) at 200 kV. The steady PL spectra and time-resolved PL decay measurements were performed using an HORIBA DeltaFlex system (HORIBA) with an excitation wavelength at 510 nm. Repetition rates were 100 and 2 MHz, respectively. The AFM data were obtained on a Dimension Icon (broker Corporation). Calibrating of roughness value, RMS, and graphics processing were taken on NanoScope Analysis. The current-voltage characteristics were measured by Keithley 2400 source and the solar simulator with standard AM 1.5G (100 mW cm<sup>-2</sup>, SSF5-3A:

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Enlitech) under ambient conditions. The *J*–V curves were measured by forward (–0.1 to 1.2 V forward bias) or reverse (1.2 to –0.1 V) scans. *J*–V curves for all devices were obtained by masking the cells with a metal mask 0.09 cm<sup>2</sup> in area. Monochromatic IPCE spectra were recorded as functions of wavelength with a monochromatic incident light of  $1 \times 10^{16}$  photons cm<sup>-2</sup> in alternating current (AC) mode with a bias voltage of 0 V (QE-R3011). The light intensity of the solar simulator was calibrated by a standard silicon solar cell provided by PV Measurements.

### **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**

energy alignment, inverted perovskite solar cells, mesoporous holetransporting layer, p-type inorganic semiconductor, stability

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