Hybrid 3D Nanostructure-Based Hole Transport Layer for Highly Efficient Inverted Perovskite Solar Cells

Dan Ouyang, Cong Chen, Zhanfeng Huang, Lu Zhu, Yanfa Yan, and Wallace C. H. Choy*

Cite This: ACS Appl. Mater. Interfaces 2021, 13, 16611–16619

ABSTRACT: In this study, we demonstrate a new hybrid three-dimensional (3D) nanostructure system as an efficient hole transport layer (HTL) by a facile design of a low-temperature solution process. It is realized by integrating high-conductive chromium-doped CuGaO₂ nanoparticles synthesized with choline chloride (denoted as Cr/CuGaO₂-CC) into ultrasmall NiOₓ nanoparticles. First, we propose to incorporate a Cr-doped strategy under hydrothermal synthesis conditions together with controllable intermediates and surfactants’ assistance to synthesize fine-sized Cr/CuGaO₂-CC nanoparticles. Subsequently, these two-dimensional (2D) nanoparticles serve as the expressway for improving hole transportation/extraction properties. Meanwhile, the ultrasmall-sized NiOₓ nanoparticles are employed to modify the surface for achieving unique surface properties. The HTL formed from the designed hybrid 3D-nanostructured system exhibits the advantages of smooth and full-covered surface, remarkable charge collection efficiency, energy level alignment between the electrode and perovskite layer, and the promotion of perovskite crystal growth. Consequently, nearly 20% of power conversion efficiency with negligible hysteresis is achieved in inverted perovskite solar cells (PSCs). This work not only demonstrates the potential applications of a 3D-nanostructured Cr/CuGaO₂-CC/NiOₓ hybrid HTL in PSCs but also provides a fundamental insight into the design of hybrid material systems by manipulating electric behavior and morphology structure for achieving high-performance photovoltaic devices.

KEYWORDS: metal oxides, nanostructure, hole transport layer, alignment band structure, perovskite solar cells

1. INTRODUCTION

Among various device configurations of perovskite solar cells (PSCs), the inverted structure (or p–i–n structure) has garnered special attention from researchers because of its negligible hysteresis effect and excellent photostability.¹,² While the recorded power conversion efficiency (PCE) of normal-type PSCs has skyrocketed to 25.2%,³,⁴ the inverted-type PSCs have a relatively low PCE of 22.3%,⁵ which asks for more efforts to further improving inverted PSCs’ performances for unlocking their full potential in photovoltaic applications. A hole transport layer (HTL), as an essential architectural component of inverted PSCs, plays significant roles in selectively extracting holes and blocking electrons⁶⁻⁹ and also greatly influences the crystallization and film quality of perovskite formed on it for improving device performances.¹⁰

Inorganic metal oxide-based HTLs, such as CuOₓ,¹⁰ NiOₓ,¹¹ NiCo₂O₄,¹² and CuCrO₂,¹³ featuring high hole mobility, good chemical stability, versatile deposition methods, and low-cost production, have been studied in PSCs. The metal oxide nanomaterials have different geometries such as two-dimensional (2D) nanoparticles and zero-dimensional (0D) nanoparticles.¹⁴⁻¹⁶ The ultrasmall 0D metal oxide nanoparticles can offer a unique advantage in forming a smooth and compact film by filling all the gaps and voids in the film. However, since the nanoparticles are typically very small with size <15 nm, holes have to travel a tortuous pathway from the nanoparticle-based HTL to the electrode, thus increasing nonradiative recombination’s probability and limiting photovoltaic performances.¹⁷ In comparison with the nanoparticles, nanostructures such as nanosheets and nanoparticles typically with less physical boundaries and lower surface defects can provide more direct conduction pathways for good charge transportation and collection.¹⁸,¹⁹,²⁰ However, the film formed from the bare nanostructure only has to concern with realizing high-quality morphology (compact, full-coverage, smooth, etc.) compared with that of nanoparticle films. We, therefore, propose to take advantage of the 0D nanoparticles and 2D nanomaterials to develop a hybrid nanostructured HTL for simultaneously realizing effective hole transportation and extraction as well as high-quality film morphologies.

Researchers have shown that graphene,²⁰ black phosphorus,²¹,²² MoS₂,²³,²⁴ SnS₂,²⁰ TiS₂,²⁵,²⁶ WS₂,²⁷ Mxene,²⁸,²⁹ Nb₂O₅,³⁰ TiO₂,³¹ and 2D perovskite...
nanesheets,\textsuperscript{32} featuring superior mechanical property, excellent tunable optoelectronic properties, and high carrier mobility with ambipolar characteristics, have been broadly investigated as carrier transport layers in PSCs. 2D nanosheet thin films not only improve the infiltration of perovskite but also effectively reduce the path to be traveled by the photogenerated charge carriers within the device and thus promote the effective collection of charge carriers. Moreover, the conclusion of the improved device performance and stability using 2D nanosheets and nanoflakes has been verified by many scientists.\textsuperscript{24,25,27,32,33} Various 2D nanostructures such as nanosheets and nanoflakes have attracted a lot of attention in nanoscale optoelectronic devices due to their unique and multifunctional properties.\textsuperscript{34,35} However, the device performance based on the bare 2D nanomaterials exhibited poor performances due to the limited conductivity and thickness.\textsuperscript{6−10} Most of them are applied as dopants or surface modification layers to improve the conductivity and tune the energy band gap of carrier-transporting layers\textsuperscript{41−45} (Table S3). Delafossite CuGaO\textsubscript{2} possesses 2D nanosheet geometry, and also, it is an interesting p-type semiconductor.\textsuperscript{46,47} Recently, it has emerged as a promising inorganic HTL material for solar cells, due to its large band gap (≈3.6 eV), relatively high hole mobility ($10^{-2}$ to $10^{-1}$ cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1}), and low valence band maximum (≈−5.3 eV).\textsuperscript{47−51} Notably, CuGaO\textsubscript{2} nanosheets synthesized from the conventional hydrothermal route usually yield large and agglomerated particles, where the diameters can be as large as from a few hundred nanometers to about 1 μm.\textsuperscript{47−50} However, big nanoparticles will cause large roughness, poor contact, and large contact resistance with the adjacent layer, which hinder their usage in inverted PSCs.

Herein, we demonstrate a new 3D-nanostructured hybrid HTL by integrating novel fine-sized Cr/CuGaO\textsubscript{2} nanoparticles synthesized with choline chloride (Cr/CuGaO\textsubscript{2−CC}) and ultrasmall NiO\textsubscript{x} nanoparticles. We propose the Cr-doped strategy in hydrothermal synthesis through controllable intermediates together with the surfactant-assisted method to synthesize CuGaO\textsubscript{2} nanoparticles with the smallest size reported so far. In the meantime, the Cr/CuGaO\textsubscript{2−CC} nanoparticles favor the integration with NiO\textsubscript{x} nanoparticles to achieve a smooth and compact surface morphology. These highly crystalline Cr/CuGaO\textsubscript{2−CC} nanoparticles serve as the expressway for hole transportation in the hybrid HTL, while ultrasmall NiO\textsubscript{x} nanoparticles provide a smooth and full-covered film morphology. The designed nanostructured Cr/CuGaO\textsubscript{2−CC}/NiO\textsubscript{x} hybrid HTL, therefore, displays a remarkable high charge extraction/collection efficiency which benefits from both the increased conductivity and suppressed recombination. Furthermore, this hybrid HTL provides good energy-band alignment between the electrode and perovskite layer to diminish the potential barrier of the carrier extraction to the electrode. Meanwhile, the noteworthy feature of low surface energy in this hybrid HTL facilitates the formation of large perovskite grains and thus reduces film defects. By employing this hybrid HTL, a nearly 20% device efficiency with negligible hysteresis is achieved in inverted PSCs. This work not only demonstrates the potential applications of 3D-structured hybrid HTLs in PSCs but also provides a new strategy to achieve highly efficient photovoltaic devices by manipulating electric behavior and morphology structure.

2. RESULTS AND DISCUSSION

2.1. Cr/CuGaO\textsubscript{2−CC} Nanoplate Synthesis and Characterization. Figure 1a shows X-ray diffraction (XRD) patterns of undoped CuGaO\textsubscript{2}, Cr/CuGaO\textsubscript{2}, and Cr/CuGaO\textsubscript{2−CC} nanocrystals. All diffraction peaks can be indexed to the delafossite CuGaO\textsubscript{2} phase (JCPDS card no. 41-0255) without other impurities. As shown in Figure 1b, the obtained nanocrystals possess the hexagonal nanoplate morphology with an average diameter of 39 nm and a thickness of 10 nm, which is much smaller than those of reported CuGaO\textsubscript{2} nanocrystals (100−200 nm).\textsuperscript{47,48,52} The high-resolution TEM (HRTEM) image of an individual Cr/CuGaO\textsubscript{2−CC} nanocrystal reveals a clear crystalline structure with a lattice spacing of about 5.7 Å, which corresponds to the (110) plane of Cr/CuGaO\textsubscript{2}.\textsuperscript{46} The selective area electron diffraction pattern (SAED, inset in Figure 1b) also confirms the pure Cr/CuGaO\textsubscript{2} phase. The elemental composition of the as-synthesized Cr/CuGaO\textsubscript{2−CC} nanocrystals is studied using scanning electron microscopy (SEM−EDS) mapping technology. It can be observed that all of the Cu, Ga, and Cr elements are homogeneously distributed, as shown in Figure S1a−c. X-ray photoelectron spectroscopy (XPS) spectra displayed in Figure S1d−f further confirm the elemental composition of the as-synthesized Cr/CuGaO\textsubscript{2−CC}. Importantly, XPS peaks located at 932.3, 1117.6, and 375.5 eV correspond to Cu\textsuperscript{2+}, Ga\textsuperscript{3+}, and Cr\textsuperscript{3+}, respectively. All the abovementioned results can verify the Cr doped into CuGaO\textsubscript{2} successfully.

The fine-sized Cr/CuGaO\textsubscript{2−CC} nanoparticles are synthesized under hydrothermal conditions by doping the Cr element, adding the surfactant, and adjusting the intermediate, which is confirmed by transmission electron microscopy and the
The histogram of nanocrystal size from more than 100 nanoparticles (Figure S2). Clearly, by introducing Cr into CuGaO$_2$, the obtained Cr/CuGaO$_2$ nanocrystals with a diameter of 48.3 nm and a thickness of 10 nm are much smaller than the undoped CuGaO$_2$ (diameter: 78.9 nm, thickness: 20 nm, Figure S2a–d), which is the smallest among reported doped CuGaO$_2$ samples. The size reduction can be explained that part of Ga atoms (0.62 Å) are easily substituted by small ionic radius Cr (0.52 Å), which is similar to other doped CuGaO$_2$. By employing a surfactant, namely, choline chloride, a further decreased size with a narrow size distribution of Cr/CuGaO$_2$-CC is observed from the statistical analysis of more than 100 nanocrystals (as shown in Figure S2e,f). The function of this surfactant is to create a barrier for nanoparticles by binding on particle surfaces and prevent the nanocrystals from growing into larger nanocrystals. Notably, from FTIR spectra shown in Figure S3, we observe a major peak at 3200 cm$^{-1}$ for the Cr/CuGaO$_2$-CC sample, indexing into the existence of remaining choline chloride (N–H stretching vibrations). It may benefit for the interaction with the following spin-coated NiO$_x$ by forming N–Ni bonds. With the assistance of the surfactant, we tune the doping concentration and collected the diameter and thickness of Cr/CuGaO$_2$ nanocrystals with different Cr-doping contents in Table S1. By increasing the Cr-doping content, the diameter CuGaO$_2$ decreases. Meanwhile, the thickness will enlarge to about 10 nm when the doping content increases to 7%.

We find that the aging time plays a critical role in determining the size of the synthesized Cr/CuGaO$_2$-CC. Figure S4 shows SEM images of the precursor before hydrothermal treatment and the corresponding final Cr/CuGaO$_2$-CC nanocrystals under different aging times (2, 6, and 10 h). It is noted that the other parameters were controlled to be the same. As shown in Figure S4a–c, there is some nanoparticle aggregation in the precursor before hydrothermal treatment. Moreover, as aging time increases, the size of the formed small granule nanoparticle grows to a thick nanosheet. XRD characterization of these precursors before hydrothermal treatment revealed that the nanoparticles formed in the beginning are Cu$_6$Cl$_4$(OH)$_8$H$_2$O intermediates (as shown in Figure S5). After a longer aging time, these intermediates transformed into CuO gradually (Figure S5).
Notably, the gerhardtite-Cu₈Cl₄(OH)₁₀H₂O intermediate phase formed by adding a Cl-containing surfactant has a high degree of dispersion. From Figure S4d−f, it is easily seen that the aging time has a strong impact on the size of the finally obtained Cr/CuGaO₂-CC nanocrystals. Especially, when the aging time increases from 6 to 10 h, the nanoplates gradually grow from 25 nm × 45 nm to 30 nm × 100 nm. Typically, Cu²⁺ ions under weak alkaline conditions promote to form intermediates due to the hydrolysis and condensation reaction. By controlling the reaction condition, the formation of intermediates with different morphologies could be adjusted. Those intermediates with aging time ranging from 2 to 6 h featuring small nanoparticle size and less aggregation morphology could convert to CuO/Cu₂O seeds within a relatively shorter time and favor to produce small-sized Cr/CuGaO₂-CC nanocrystals in the subsequent hydrothermal treatment. Consequently, the abovementioned results illustrate that the strategy of (1) doping Cr, (2) adding the surfactant, and (3) adjusting the intermediate in the successful synthesis allows us to demonstrate fine-sized CuGaO₂ nanocrystal nanoplates.

2.2. Inverted PSCs with a 3D-Nanostructured Hybrid HTL. Regarding the film of the hybrid nanostructured HTL, we first spin-coated a Cr/CuGaO₂-CC film on ITO, where the top SEM image is shown in Figure S6b. From the atomic force microscopy (AFM) image shown in Figure S6e, the Cr/CuGaO₂-CC film exhibits a root mean square (RMS) roughness value of about 23 nm. With ultrasmall NiOₓ nanoparticles (Figure S6a,d), the proposed novel 3D-nanostructured Cr/CuGaO₂-CC/NiOₓ film with an RMS of about 14 nm (Figure S6f) was prepared via a room-temperature solution process method, where the corresponding SEM image is shown in Figure S6c.

To investigate the effects of this 3D-nanostructured Cr/CuGaO₂-CC/NiOₓ film as an HTL, we fabricate inverted PSCs with the configuration of ITO/Cr/CuGaO₂-CC/NiOₓ/MAPbI₃−ₓClₓ/PC₆₁BM/C₆₀/ZrAcac/Ag (shown in Figure 2a). The energy-level diagram of various functional layers in the PSCs is shown in Figure 2b, where the energy levels of CH₃NH₃PbI₃−ₓClₓ, PC₆₁BM/C₆₀, ZrAcac, and Ag are collected from the literature, and the energy level of Cr/CuGaO₂-CC is calculated using ultraviolet photoelectron spectroscopy (UPS) and ultraviolet−visible (UV−vis) spectroscopy, which will be discussed in detail later. The current density−voltage (J−V) characteristics of the optimized PSCs under the illumination of AM 1.5 G, 100 mW cm⁻² are presented in Figure 2c. The champion PSCs with a NiOₓ/Cr/CuGaO₂-CC HTL offer a V_OC of 1.08 V, a J_SC of 22.93 mA cm⁻², an FF of 0.81, and a PCE of 19.91% under a forward scan direction. It exhibits about 11% enhancement compared to the control device based on NiOₓ including a V_OC of 1.08 V, a J_SC of 22.02 mA cm⁻², an FF of 0.75, and a PCE of 17.91% (shown in Figure S7). The improvement of the device efficiency is mainly attributed to significantly enhanced J_SC and FF, which is contributed by the reduced transport path and enhanced hole extraction of the Cr/CuGaO₂-CC/NiOₓ HTL. The negligible hysteresis curves of Cr/CuGaO₂-CC/NiOₓ-based PSCs, as shown in Figure 2d, indicate the good contact between the HTL and perovskite layer, which is better than that of NiOₓ (17.91%) and Cr/CuGaO₂-CC (14.96%) HTL-based PSCs (Table S2). Steady-state output efficiency measured at the maximum power point voltage (V_mpp) is then studied to verify the reliability of the device performance, as shown in Figure 2e. After the illumination under 1 sun for 200 s, the stabilized photocurrent and PCE remain 21.61 mA cm⁻² and 19.71% at 0.912 V, respectively, agreeing well with the values measured

Figure 3. (a) Absorption spectra of perovskite growth on NiOₓ and Cr/CuGaO₂-CC/NiOₓ HTLs. (b) Transmission spectra of NiOₓ and Cr/CuGaO₂-CC/NiOₓ HTLs. (c) UPS spectrum of the spin-coated Cr/CuGaO₂-CC/NiOₓ film.
from $J−V$ curves (Figure 2d). However, it is found that the reproducibility of Cr/CuGaO$_2$-CC/NiO$_x$ HTL-based PSCs is slightly poor than that of the NiO$_x$ HTL due to the size effect of Cr/CuGaO$_2$-CC on the film uniformity, as shown in Figure S10.

### 2.3. Effects of the 3D-Nanostructured Hybrid HTL on Inverted PSCs.

The incident photo-to-electron conversion efficiency (IPCE) spectra and the calculated $J_{SC}$ of the corresponding device are displayed in Figure 2f. The integrated $J_{SC}$ of the optimized devices is 21.90 and 20.80 mA cm$^{-2}$ for solar cells based on Cr/CuGaO$_2$-CC/NiO$_x$ and NiO$_x$, respectively, which are consistent with the value determined by the $J−V$ measurement (see Figure 2d). Compared to NiO$_x$-based control devices, the IPCE of the Cr/CuGaO$_2$-CC/NiO$_x$-based device is higher in the wavelength range from 350 to 500 nm. Similar results are obtained from the UV–vis absorption of the NiO$_x$ and Cr/CuGaO$_2$-CC/NiO$_x$-coated perovskite films, as shown in Figure 3a. The intensity of light absorption of the Cr/CuGaO$_2$-CC/NiO$_x$-coated perovskite layers is slightly higher in the range of 300–500 nm, which is attributed to the light-scattering effect of large-sized Cr/CuGaO$_2$-CC nanocrystals inside the Cr/CuGaO$_2$-CC/NiO$_x$ HTL; IPCE and $J_{SC}$ thus improve. Furthermore, a slightly enhanced transmission of the Cr/CuGaO$_2$-CC/NiO$_x$ HTL than NiO$_x$ also contributes to the increased $J_{SC}$ as shown in Figure 3b.

To dig out the reasons for the improved device performance, we investigate the electrical properties of the Cr/CuGaO$_2$-CC/NiO$_x$ HTL. From the photoelectron spectroscopy (UPS) spectra, the valence band maximum (VBM) of the Cr/CuGaO$_2$-CC film is estimated to be $−5.22$ eV, as shown in Figure 3c. Interestingly, introducing Cr/CuGaO$_2$-CC into a NiO$_x$ layer to form 3D-structured Cr/CuGaO$_2$-CC/NiO$_x$ could form band-alignment energy level between NiO$_x$ and ITO, favoring hole transfer from NiO$_x$ to ITO. Meanwhile, the corresponding CBM is deduced to be $−1.68$ eV by UPS and UV–vis absorption spectroscopy. From the band-alignment energy-level diagram in Figure 2b, we observe that the VBM of Cr/CuGaO$_2$-CC/NiO$_x$ is a fairly well-matched energy level with the VBM of CH$_3$NH$_3$PbI$_{3−x}$Cl$_x$ ($−5.40$ eV); simultaneously, the conducting band maximum (CBM) is above the CBM of the perovskite film, which is prerequisite to achieving excellent device performance. Hence, the designed 3D-nanostructured hybrid HTL not only makes it efficient to extract the photoinduced holes from the perovskite into the HTL and then transport to the electrode but also makes it beneficial for block electrons from injection into the HTL.

The conductivity of the NiO$_x$ and Cr/CuGaO$_2$-CC/NiO$_x$ is studied by measuring the $J−V$ curves across an ITO/HTL (NiO$_x$ or Cr/CuGaO$_2$-CC/NiO$_x$)/Ag test structure (as illustrated in Figure 4a). It is found that the Cr/CuGaO$_2$-CC/NiO$_x$ film shows enhanced conductivity compared to the NiO$_x$ film. It may be because the fabricated 3D-structured Cr/CuGaO$_2$-CC/NiO$_x$ film can provide a direct channel for hole transfer rather than the zigzag pathway between NiO$_x$ nanoparticles, which accelerates the hole transport inside the HTL. Moreover, the increase in the hole transport properties was further proved from hole-only devices with the ITO/HTL (NiO$_x$ or Cr/CuGaO$_2$-CC/NiO$_x$)/MoO$_3$/Ag device configuration using the SCLC model (Figure 4b). The $J−V$ curves show that the Cr/CuGaO$_2$-CC/NiO$_x$ film exhibited higher current density at the same forward bias than the NiO$_x$ film, indicating the better capability of hole extraction and transport of the Cr/CuGaO$_2$-CC/NiO$_x$.

To further illustrate the hole extraction ability of HTL materials, we conduct PL and TRPL for CH$_3$NH$_3$PbI$_{3−x}$Cl$_x$ films coated on glass, NiO$_x$, and Cr/CuGaO$_2$-CC/NiO$_x$ film.
The work function of ITO (4.70 eV) is between the perovskite emission, and the 3D-nanostructured hybrid HTL depicts stronger quenching compared with NiO. These results demonstrate that the formation of a 3D-structured system with better band-alignment energy levels plays a positive role in facilitating the hole extraction and transfer from perovskite to the HTMs; thus, superior hole collection could be expected for 3D-nanostructured hybrid HTL-based PSCs. The improved hole extraction and transport properties can be further confirmed by TRPL spectroscopy, as shown in Figure 4d, where all curves are fitted using the two-component exponential decay model. The average PL lifetime of perovskite on the NiO HTL is 86 ns and sharply reduced to 55 ns for the Cr/CuGaO2-CC/NiO HTL, meaning a more rapid hole injection and transfer capability of the Cr/CuGaO2-CC/NiO HTL than that of the NiO HTL. The quick charger transfer of the Cr/CuGaO2-CC/NiO HTL is mainly attributed to the higher electrical conductivity and the cascade energy alignment via dividing the energy difference between the work function of ITO (4.70 eV) and NiO (5.25 eV), facilitating quick hole transport from the perovskite layer to the anode. As mentioned previously, holes may need more time to pass through the NiO film than the 3D-nanostructured CuGaO2-CC/NiO layer and increase the possibility of unwanted internal recombination. The suppressed charge recombination in the 3D-structured Cr/CuGaO2-CC/NiO HTL is beneficial for effectively improving device performance.

In order to examine the effect of the suppressed recombination process on the PSC performance, we compare the dark J–V characteristics of Cr/CuGaO2-CC/NiO and NiO-based PSCs, as shown in Figure S8. The dark J–V characteristics show that the Cr/CuGaO2-CC/NiO-based device achieved a lower leakage current density in the diffusion-dominated region at reverse bias and a lower positive bias compared with NiO-based devices, indicating the excellent blocking electron injection from ITO to Cr/CuGaO2-CC/NiO HTL. The blocking electron injection originates from the large electron injection barrier of 3.06 eV between ITO and Cr/CuGaO2-CC/NiO HTL (shown in Figure 2b).

It is well-known that film formation and surface morphology of the CH3NH3PbI3−xClx absorber layer are crucial for the device performance. From the top-view SEM image (Figure 5a,b), it can be seen that the average grain sizes of perovskite on Cr/CuGaO2-CC/NiO are relatively larger than that grown on NiO, which may be caused by the depressed heterogenous nucleation on the more hydrophobic surface (contact angle inserted in Figure 5c,d). The increased crystallinity can be further demonstrated by the XRD patterns in Figure S9. The intensity of two strong peaks at 14.5° and 28.4°, which are indexed to (110) and (220) of perovskite, is similar to that of the Cr/CuGaO2-CC/NiO film than NiO films. However, there is a smaller full width at half maxima (FWHM) for the perovskite film on the Cr/CuGaO2-CC/NiO HTL than that of the pristine NiO HTL, indicating a bigger crystal size on the Cr/CuGaO2-CC/NiO HTL, which is consistent with the result from the SEM image (as shown in Figure 5). Consequently, these highly efficient PSCs based on the Cr/CuGaO2-CC/NiO HTL is mainly attributed to the promoted perovskite grain growth and very good electrical properties of the Cr/CuGaO2-CC/NiO film, which support the superiority of the 3D-structured Cr/CuGaO2-CC/NiO HTL for achieving high-efficiency PSC devices.

Nowadays, stability is also a very important factor in this field. Here, the storage stability for PSCs with NiO and Cr/CuGaO2-CC/NiO as the HTL is shown in Figure S11. When all sample devices’ storage under a N2 condition without encapsulation for two months is studied, the PCE of Cr/CuGaO2-CC/NiO HTL-based PSCs almost remains unchanged, while that of the NiO HTL-based reference devices just remains 80% of the original PCE. The improved stability for Cr/CuGaO2-CC/NiO HTL-based PSCs can be explained by the improved perovskite film, which agrees with the results in Figure 5.

3. CONCLUSIONS

In summary, we demonstrate a new 3D-nanostructured hybrid HTL by introducing fine-sized 2D Cr/CuGaO2 nanoparticles and ultrasmall 0D NiO nanoparticles, which offers the effective transportation and extraction of holes as well as high film quality. We propose the Cr-doped strategy under a hydrothermal condition together with controlled surfactant-assisted intermediates to synthesize the smallest size Cr/CuGaO2 nanoparticles reported. By integrating with ultrasmall NiO nanoparticles, a room-temperature solution-processed 3D-nanostructured Cr/CuGaO2-CC/NiO film is formed. The HTL features enhanced conductivity, more efficient charge transport ability, more favorable energy-level alignment, and promoted the perovskite crystal growth as compared to the pristine material counterparts of NiO and Cr/CuGaO2-CC. The inverted PSCs based on this hybrid HTL obtain a PCE of 19.91% with negligible hysteresis, outperforming those of standard reference PSCs based on the pristine NiO nanoparticle HTL (the highest PCE = 17.60%). Consequently, our work not only demonstrates a promising 3D-structured Cr/CuGaO2-CC/NiO HTL for high-performance PSCs but also provides a new strategy to design efficient metal oxide nanocomposite-based CTLs for high-efficiency photovoltaic devices.
4. EXPERIMENTAL SECTION

4.1. Materials. All chemicals with analytical reagent grade were used as received unless otherwise noted. Gallium nitrate hydrate (Ga(NO₃)₃·xH₂O, 99.99%) and chromium (III) nitrate nonhydrate (Cr(NO₃)₃, 99%) were purchased from Strem Chemicals, Inc. Ethylene glycol (EG, 99.8%) was purchased from Sigma-Aldrich. Choline chloride (CC, 98%) and copper (II) nitrate trihydrate (Cu(NO₃)₂·3H₂O, 99%) were purchased from JK Science. Besides, for other similar chemicals, refer to our previous works.²,¹²

4.2. Synthesis of Cr/CuGaO₂-CC Nanoplates. 0.6 mmol Cu(NO₃)₂·3H₂O, 0.6−x mmol Ga(NO₃)₃·xH₂O, x mmol Cr(NO₃)₃·xH₂O, and 240 mg of CC were mixed in 3 mL of deionized (DI) water and 3 mL of EG with stirring for 10 min. Then, 0.5 M KOH solution was added dropwise to adjust the pH value to 8 in an ice bath. After stirring at ambient for 2 h, the prepared solution was transferred into a 20 mL Teflon-lined autoclave and kept at 250 °C in an oven for 2 h. The precipitate was collected after cooling down to room temperature and washing with dilute aqueous ammonia solution and dilute HNO₃ solution in sequence several times to remove the impurity. After washing with DI water and ethanol, the obtained nanocrystals were finally stored in isopropanol for further use.

4.3. Preparation of HTL Films and Fabrication of Devices. Cr/CuGaO₂-CC isopropanol suspension (5% doping level, 25 mg/mL) was spin-coated on ultraviolet ozone-treated ITO substrates at 2000 rpm by two times. The NiO₉ solution was prepared according to our previous report¹¹ and then spin-coated on top of the Cr/CuGaO₂-CC layer at 2000 rpm. For comparison, the bare NiO₉ film was also formed. For the detailed device fabrication process, refer to our previous work.¹²

4.4. Characterization and Measurement. For all similar measurement and the corresponding equipment, refer to our previous works.²,⁶¹

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c21064.

Characterization of materials and perovskite solar cells (PDF)

AUTHOR INFORMATION

Corresponding Author
Wallace C. H. Choy — Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 999077, China; orcid.org/0000-0002-9535-4076; Email: chchoy@eee.hku.hk

Authors
Dan Ouyang — Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 999077, China
Cong Chen — Department of Physics and Astronomy, and Wright Center for Photovoltaics Innovation and Commercialization (PVTC), University of Toledo, Toledo, Ohio 43606, United States; orcid.org/0000-0003-2692-1871
Zhanfeng Huang — Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 999077, China
Lu Zhu — Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong 999077, China
Yanfa Yan — Department of Physics and Astronomy, and Wright Center for Photovoltaics Innovation and Commercialization (PVTC), University of Toledo, Toledo, Ohio 43606, United States; orcid.org/0000-0003-3977-5789

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsami.0c21064

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported by the University Grant Council of the University of Hong Kong (grant# 201811159147, and Research Equipment Fund), the General Research Fund (grant 17200518, 17201819, and 17211220) and Collaborative Research Grant (C7035-20G) from the Research Grants Council (RGC) of Hong Kong Special Administrative Region, China, and the Environment Conservation Fund of ECF Project 64/2018.

REFERENCES


