

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

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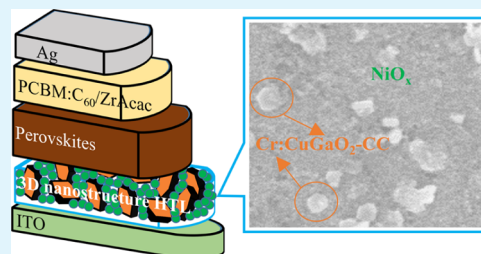
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ABSTRACT: In this study, we demonstrate a new hybrid three-dimensional (3D) nanostructure system as an efficient hole transport layer (HTL) by a facile design of a low-temperature solution process. It is realized by integrating high-conductive chromium-doped CuGaO_2 nanoplates synthesized with choline chloride (denoted as $\text{Cr/CuGaO}_2\text{-CC}$) into ultrasmall NiO_x 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 $\text{Cr/CuGaO}_2\text{-CC}$ nanoplates. Subsequently, these two-dimensional (2D) nanoplates serve as the expressway for improving hole transportation/extraction properties. Meanwhile, the ultrasmall-sized NiO_x 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 $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ 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 electrons^{6–9} and also greatly influences the crystallization and film quality of perovskite formed on it for improving device performances.

Inorganic metal oxide-based HTLs, such as CuO ,¹⁰ NiO ,¹¹ NiCo_2O_4 ,¹² and CuCrO_2 ,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) nanoplates 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,

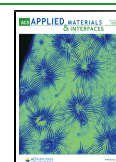
holes have to travel a tortuous pathway from the nanoparticle-based HTL to the electrode, thus increasing nonradiative recombination's probability and limiting photovoltaic performances.¹⁷ In comparison with the nanoparticles, nanostructures such as nanosheets and nanoplates typically with less physical boundaries and lower surface defects can provide more direct conduction pathways for good charge transportation and collection.^{18,19} 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 nanoplates to develop a hybrid nanostructured HTL for simultaneously realizing effective hole transportation and extraction as well as high-quality film morphologies.

Recently, 2D nanosheets and nanoflake materials, such as graphene,²⁰ black phosphorus,^{21,22} MoS_2 ,^{23,24} SnS_2 ,²⁰ TiS_2 ,^{25,26} WS_2 ,²⁷ Mxene ,^{28,29} Nb_2O_5 ,³⁰ TiO_2 ,³¹ and 2D perovskite

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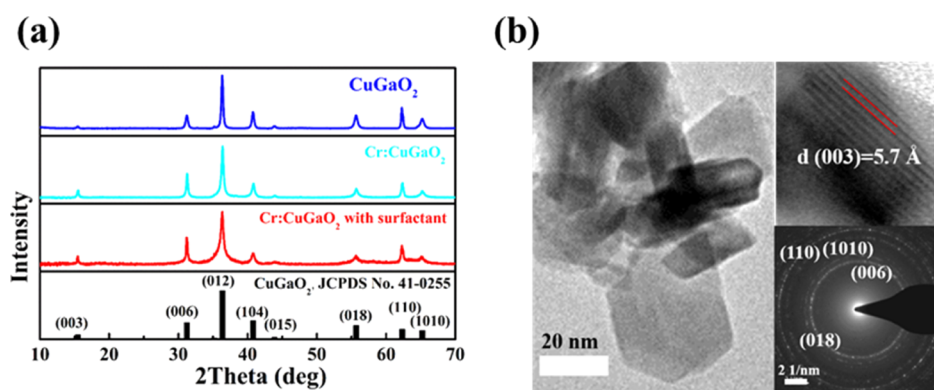


Figure 1. (a) XRD patterns of the as-synthesized CuGaO_2 , Cr/CuGaO_2 , and $\text{Cr/CuGaO}_2\text{-CC}$ NPs. (b) HRTEM image and indexed SAED pattern of the as-synthesized $\text{Cr/CuGaO}_2\text{-CC}$ NPs.

nanosheets,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.^{24,25,27,32,33} Various 2D nanostructures such as nanosheets and nanoplates have attracted a lot of attention in nanoscale optoelectronic devices due to their unique and multifunctional properties.^{34,35} However, the device performance based on the bare 2D nanomaterials exhibited poor performances due to the limited conductivity and thickness.^{36–40} 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^{41–45} (Table S3). Delafossite CuGaO_2 possesses 2D nanoplate geometry, and also, it is an interesting p-type semiconductor.^{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 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$), and low valence band maximum (~ -5.3 eV).^{47–51} Notably, CuGaO_2 nanoplates 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 $1 \mu\text{m}$.^{47–50} However, big nanoplates 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_2 nanoplates synthesized with choline chloride ($\text{Cr/CuGaO}_2\text{-CC}$) and ultrasmall NiO_x nanoparticles. We propose the Cr-doped strategy in hydrothermal synthesis through controllable intermediates together with the surfactant-assisted method to synthesize CuGaO_2 nanoplates with the smallest size reported so far. In the meantime, the $\text{Cr/CuGaO}_2\text{-CC}$ nanoplates favor the integration with NiO_x nanoparticles to achieve a smooth and compact surface morphology. These highly crystalline $\text{Cr/CuGaO}_2\text{-CC}$ nanoplates serve as the expressway for hole transportation in the hybrid HTL, while ultrasmall NiO_x nanoparticles provide a smooth and full-covered film morphology. The designed nanostructured $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ 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. $\text{Cr/CuGaO}_2\text{-CC}$ Nanoplate Synthesis and Characterization. Figure 1a shows X-ray diffraction (XRD) patterns of undoped CuGaO_2 , Cr/CuGaO_2 , and $\text{Cr/CuGaO}_2\text{-CC}$ nanocrystals. All diffraction peaks can be indexed to the delafossite CuGaO_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_2 nanocrystals (100–200 nm).^{47,48,52} The high-resolution TEM (HRTEM) image of an individual $\text{Cr/CuGaO}_2\text{-CC}$ nanocrystal reveals a clear crystalline structure with a lattice spacing of about 5.7 Å, which corresponds to the (110) plane of Cr/CuGaO_2 .⁴⁶ The selective area electron diffraction pattern (SAED, inset in Figure 1b) also confirms the pure Cr/CuGaO_2 phase. The elemental composition of the as-synthesized $\text{Cr/CuGaO}_2\text{-CC}$ nanoplates 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 $\text{Cr/CuGaO}_2\text{-CC}$. Importantly, XPS peaks located at 932.3, 1117.6, and 375.5 eV correspond to Cu^+ , Ga^{3+} , and Cr^{3+} , respectively. All the abovementioned results can verify the Cr doped into CuGaO_2 successfully.

The fine-sized $\text{Cr/CuGaO}_2\text{-CC}$ nanoplates 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

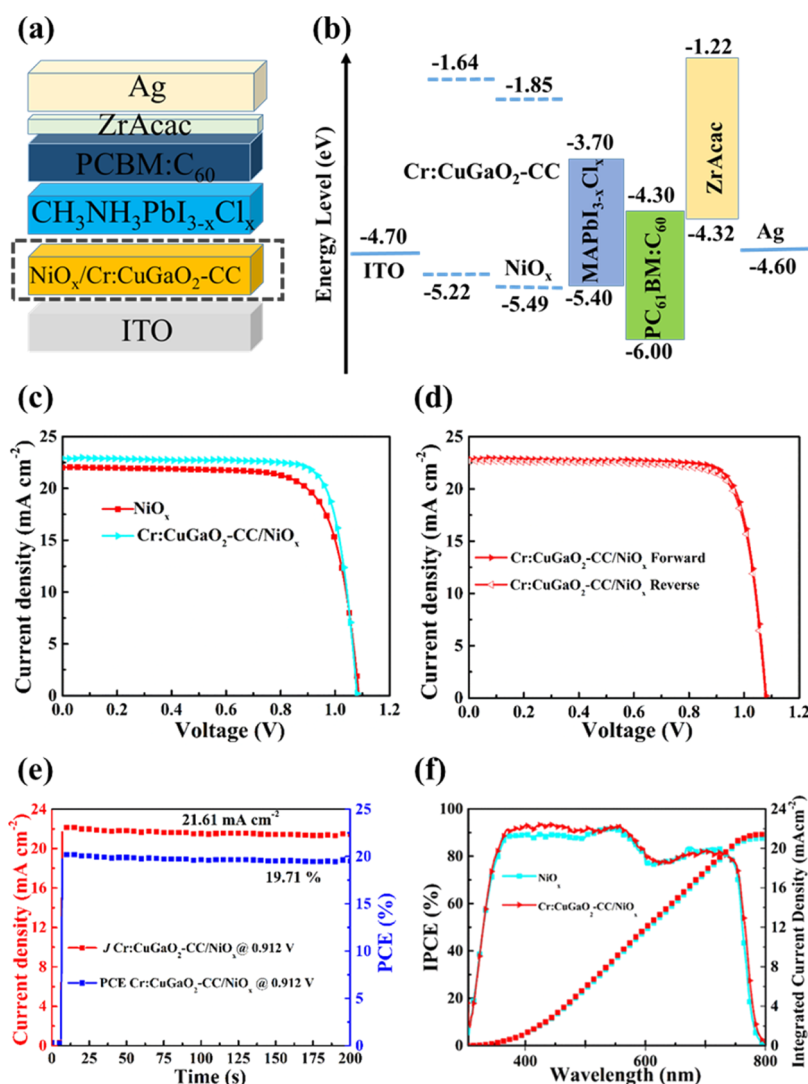


Figure 2. (a) Device structure. (b) Energy-level diagram. (c) J - V characteristics of the best NiO_x - and $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ -based PSCs measured under AM 1.5 G 100 mW cm^{-2} illumination. (d) J - V characteristics of devices extracted from forward and reverse sweeping based on the $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTL. (e) Steady photocurrent (red) and PCE (blue) under 1 sun illumination of the best $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTL-based PSCs. (f) IPCE spectra and the calculated J_{SC} of NiO_x and $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTL-based PSCs.

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 .⁵³ By employing a surfactant, namely, choline chloride, a further decreased size with a narrow size distribution of $\text{Cr/CuGaO}_2\text{-CC}$ 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 $\text{Cr/CuGaO}_2\text{-CC}$ 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.^{54,55} 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 $\text{Cr/CuGaO}_2\text{-CC}$. Figure S4 shows SEM images of the precursor before hydrothermal treatment and the corresponding final $\text{Cr/CuGaO}_2\text{-CC}$ 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 $\text{Cu}_9\text{Cl}_4(\text{OH})_{10}\text{H}_2\text{O}$ intermediates (as shown in Figure S5). After a longer aging time, these intermediates transformed into CuO gradually (Figure S5).

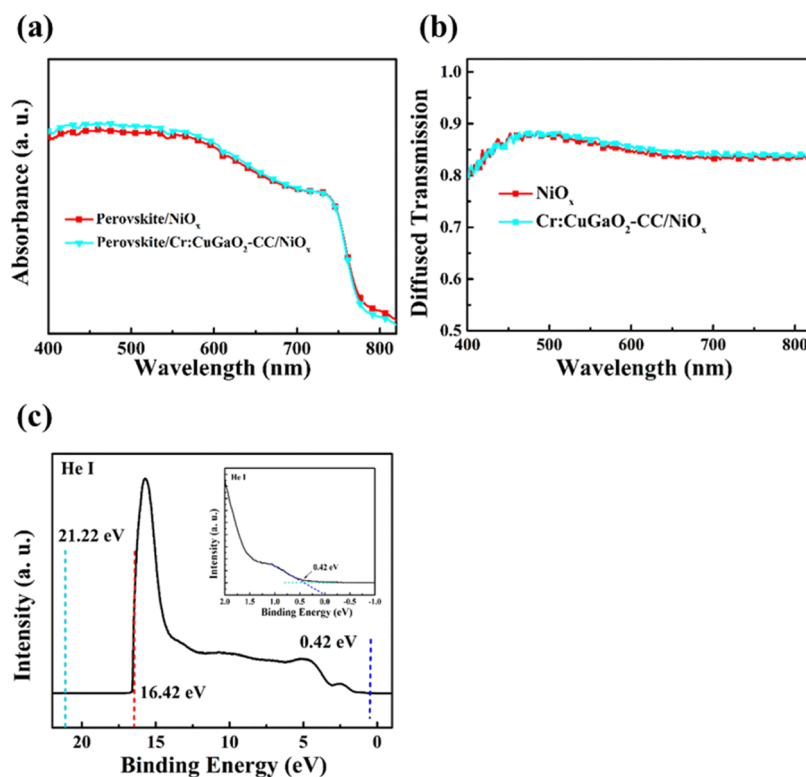


Figure 3. (a) Absorption spectra of perovskite growth on NiO_x and $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTLs. (b) Transmission spectra of NiO_x and $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTLs. (c) UPS spectrum of the spin-coated $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ film.

Notably, the gerhardtite- $\text{Cu}_9\text{Cl}_4(\text{OH})_{10}\text{H}_2\text{O}$ 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 $\text{Cr/CuGaO}_2\text{-CC}$ nanocrystals. Especially, when the aging time increases from 6 to 10 h, the nanoplates gradually grow from $25\text{ nm} \times 45\text{ nm}$ to $30\text{ nm} \times 100\text{ nm}$. Typically, Cu^{2+} ions under weak alkaline conditions promote to form intermediates due to the hydrolysis and condensation reaction.⁵⁶ 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 $\text{CuO/Cu}_2\text{O}$ seeds within a relatively shorter time⁵² and favor to produce small-sized $\text{Cr/CuGaO}_2\text{-CC}$ 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 CuGaO_2 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 $\text{Cr/CuGaO}_2\text{-CC}$ 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 $\text{Cr/CuGaO}_2\text{-CC}$ film exhibits a root mean square (RMS) roughness value of about 23 nm. With ultrasmall NiO_x nanoparticles (Figure S6a,d), the proposed novel 3D-nanostructured $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ 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 $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ film as an HTL, we fabricate inverted PSCs with the configuration of $\text{ITO/Cr/CuGaO}_2\text{-CC/NiO}_x/\text{MAPbI}_{3-x}\text{Cl}_x/\text{PCBM}/\text{C}_{60}/\text{ZrAcac}/\text{Ag}$ (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 $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$, $\text{PC}_{61}\text{BM}/\text{C}_{60}$, ZrAcac , and Ag are collected from the literature,^{57,58} and the energy level of $\text{Cr/CuGaO}_2\text{-CC}$ 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 $\text{NiO}_x/\text{Cr/CuGaO}_2\text{-CC}$ 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 NiO_x , 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 $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTL. The negligible hysteresis curves of $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ -based PSCs, as shown in Figure 2d, indicate the good contact between the HTL and perovskite layer,⁵⁹ which is better than that of NiO_x (17.91%) and $\text{Cr/CuGaO}_2\text{-CC}$ (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

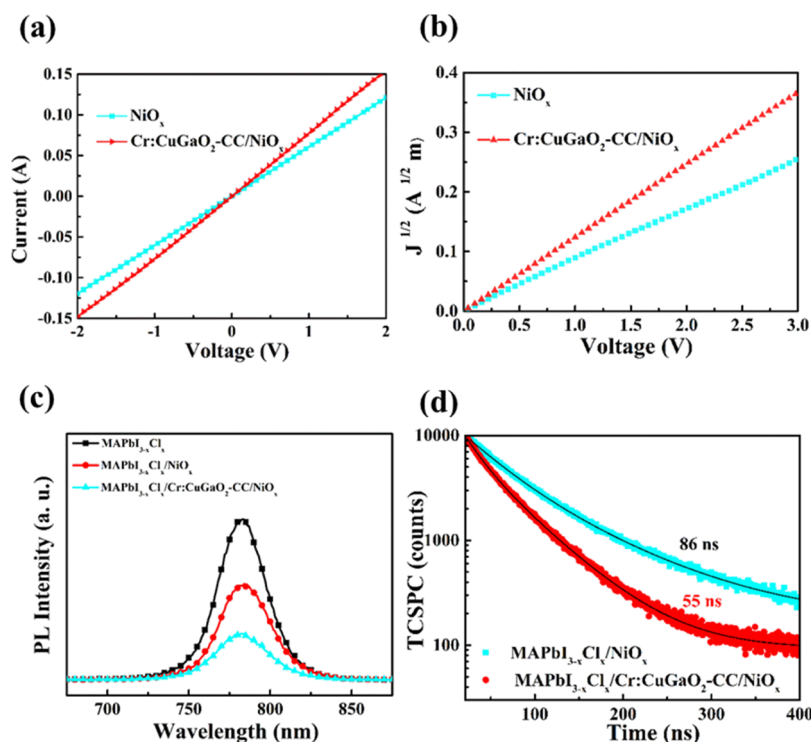


Figure 4. (a) I – V curves of ITO/ NiO_x /Ag and ITO/Cr/CuGaO₂-CC/ NiO_x /Ag diodes. (b) J – V curve of the hole-only devices with the ITO/HTL(NiO_x or Cr/CuGaO₂-CC/ NiO_x)/MoO₃/Ag structure. (c) PL and (d) TRPL spectra of the perovskite on NiO_x and Cr/CuGaO₂-CC/ NiO_x HTL, respectively.

from J – V curves (Figure 2d). However, it is found that the reproducibility of Cr/CuGaO₂-CC/ NiO_x HTL-based PSCs is slightly poor than that of the NiO_x HTL due to the size effect of Cr/CuGaO₂-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/CuGaO₂-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/CuGaO₂-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/CuGaO₂-CC/ NiO_x -coated perovskite films, as shown in Figure 3a. The intensity of light absorption of the Cr/CuGaO₂-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/CuGaO₂-CC nanocrystals inside the Cr/CuGaO₂-CC/ NiO_x HTL; IPCE and J_{SC} thus improve. Furthermore, a slightly enhanced transmission of the Cr/CuGaO₂-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 performances, we investigate the electrical properties of the Cr/CuGaO₂-CC/ NiO_x HTL. From the photoelectron spectroscopy (UPS) spectra, the valence band maximum (VBM) of the Cr/CuGaO₂-CC film is estimated to be −5.22 eV, as shown in Figure 3c. Interestingly, introducing Cr/CuGaO₂-CC into a NiO_x layer to form 3D-structured Cr/CuGaO₂-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/CuGaO₂-CC/ NiO_x is a fairly well-matched energy level with the VBM of $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ (−5.40 eV);¹² 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/CuGaO₂-CC/ NiO_x is studied by measuring the I – V curves across an ITO/HTL (NiO_x or Cr/CuGaO₂-CC/ NiO_x)/Ag test structure (as illustrated in Figure 4a). It is found that the Cr/CuGaO₂-CC/ NiO_x film shows enhanced conductivity compared to the NiO_x film. It may be because the fabricated 3D-structured Cr/CuGaO₂-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/CuGaO₂-CC/ NiO_x)/MoO₃/Ag device configuration using the SCLC model (Figure 4b). The J – V curves show that the Cr/CuGaO₂-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/CuGaO₂-CC/ NiO_x .

To further illustrate the hole extraction ability of HTL materials, we conduct PL and TRPL for $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ films coated on glass, NiO_x , and Cr/CuGaO₂-CC/ NiO_x film

substrates, respectively, as shown in Figure 4c. It is clear that both NiO_x and $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ interlayer quenched the perovskite emission, and the 3D-nanostructured hybrid HTL depicts stronger quenching compared to that of the NiO_x film. 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.⁶⁰ The average PL lifetime (τ_{ave}) of perovskite on the NiO_x HTL is 86 ns and sharply reduced to 55 ns for the $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTL, meaning a more rapid hole injection and transfer capability of the $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTL than that of the NiO_x HTL. The quick charger transfer of the $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ 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_x (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_x nanoparticle film than the 3D-nanostructured $\text{CuGaO}_2\text{-CC/NiO}_x$ layer and increase the possibility of unwanted internal recombination. The suppressed charge recombination in the 3D-structured $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ 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 $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ - and NiO_x -based PSCs, as shown in Figure S8. The dark J - V characteristics show that the $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ -based device achieved a lower leakage current density in the diffusion-dominated region at reverse bias and a lower positive bias compared with NiO_x -based devices, indicating the excellent blocking electron injection from ITO to $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTL. The blocking electron injection originates from the large electron injection barrier of 3.06 eV between ITO and $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTL (shown in Figure 2b).

It is well-known that film formation and surface morphology of the $\text{CH}_3\text{NH}_3\text{PbI}_{3-x}\text{Cl}_x$ 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 $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ are relatively larger than that grown on NiO_x , which may be caused by the suppressed heterogeneous 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 $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ film than NiO_x films. However, there is a smaller full width at half maxima (FWHM) for the perovskite film on the $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTL than that of the pristine NiO_x HTL, indicating a bigger crystal size on the $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTL, which is consistent with the result from the SEM image (as shown in Figure 5). Consequently, these highly efficient PSCs based on the $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTL is mainly attributed to the promoted perovskite grain growth and very good electrical properties of the $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ film, which support

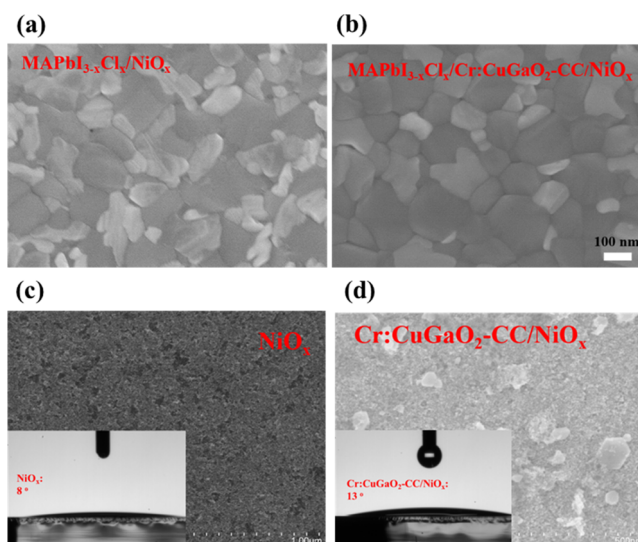


Figure 5. SEM images of perovskite formed on (a) NiO_x and (b) $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTL, respectively. SEM images of (c) NiO_x and (d) $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTL, where contact angles are inserted in the images, respectively.

the superiority of the 3D-structured $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ 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_x and $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ as the HTL is shown in Figure S11. When all sample devices' storage under a N_2 condition without encapsulation for two months is studied, the PCE of $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ HTL-based PSCs almost remains unchanged, while that of the NiO_x HTL-based reference devices just remains 80% of the original PCE. The improved stability for $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ 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/CuGaO_2 nanoplates and ultrasmall 0D NiO_x 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/CuGaO_2 nanoplates reported. By integrating with ultrasmall NiO_x nanoparticles, a room-temperature solution-processed 3D-nanostructured $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ 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_x and $\text{Cr/CuGaO}_2\text{-CC}$. 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_x nanoparticle HTL (the highest PCE = 17.60%). Consequently, our work not only demonstrates a promising 3D-structured $\text{Cr/CuGaO}_2\text{-CC/NiO}_x$ 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 ($\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, 99.99%) and chromium (III) nitrate nonhydrate ($\text{Cr}(\text{NO}_3)_3$, 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 ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 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 $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 0.6- x mmol $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$, x mmol $\text{Cr}(\text{NO}_3)_3$, 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 HNO_3 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 NiO_x 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 NiO_x 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.^{12,61}

■ ASSOCIATED CONTENT

SI 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)

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Notes

The authors declare no competing financial interest.

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