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Work-Function-Tunable Electron Transport Layer of Molecule-Capped Metal Oxide for a High-Efficiency and Stable p-i-n Perovskite Solar Cell

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ABSTRACT: The composite electron transporting layer (ETL) of metal oxide with [6,6]-phenyl- C_{61} -butyric acid methyl ester (PCBM) prevents perovskite from metal electrode erosion and increases p-i-n perovskite solar cell (PVSC) stability. Although the oxide exhibits protective function, an additional work function modifier is still needed for good device performance. Usually, complicated multistep synthesis is employed to have a highly crystalline film that increases manufacturing cost and inhibits scalability. We report a facile synthesis of a novel organic-molecule-capped metal oxide nanoparticle film for the composite ETL. The nanoparticle film not only has a dual function of electron transport and protection but also exhibits work function tunability. Solvothermal-prepared SnO₂ nanoparticles are capped with tetrabutylammonium hydroxide (TBAOH) through ligand exchange. The resulting TBAOH–SnO₂ nanoparticles disperse well in ethanol and form a uniform film on PCBM. The power conversion efficiency of the device dramatically increases from 14.91 to 18.77% using this layer because of reduced charge accumulation and aligned band structure. The PVSC thermal stability is significantly enhanced by adopting this layer, which prevents migration of I⁻ and Ag. The ligand exchange method extends to other metal oxides, such as TiO₂, ITO, and CeO₂, demonstrating its broad applicability. These results provide a cornerstone for large-scale manufacture of high-performance and stable PVSCs.

KEYWORDS: perovskite solar cell, work function modifier, metal oxide nanoparticle, ligand exchange, electron transport layer

■ INTRODUCTION

Organic and inorganic perovskite solar cells (PVSCs) are regarded as the most promising third-generation photovoltaic technology toward commercialization due to their advantages of low manufacturing cost, solution processability, and high power conversion efficiency (PCE). Recently, the highest certified PCE of PVSCs has reached 25.2%.¹ Until now, various architectures of PVSCs have been developed, including mesoporous n-i-p,² planar n-i-p,³ and planar p-i-narchitectures.⁴ Among these architectures, the planar architecture is more favorable for commercialization due to its ease of fabrication, hysteresis-free, and low cost. The planar p-i-nPVSCs have a structure of glass/FTO or ITO/hole transport layer (HTL)/perovskite layer/electron transport layer (ETL)/ Au, Ag, or Al.^{5,6} Many p-type organic and inorganic materials, such as poly(3,4-ethylenedioxythiophene) (PEDOT:PSS),^{7–9} poly(triarylamine) (PTAA),^{10,11} and nickel oxide (NiO_x),^{12,13} were investigated for the HTLs of the p–i–n PVSCs. Among these HTLs, NiO_x attracts the most attention due to its low processing temperature, high transmittance in the visible region, deep valence band edge, and high conductivity. The fullerene derivative, [6,6]-phenyl-C₆₁-butyric acid methyl ester

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(PCBM), is the most common ETL to transport electrons and to effectively passivate the defects of the perovskite layer.^{14–16} To obtain high-PCE PVSCs, it is critical to employ a suitable ETL and HTL to efficiently transport the charge carriers and reduce the charge recombination.^{17,18} In addition to the high PCE, the stability of PVSCs is also important to become a commercially viable product.

Recently, several groups have reported different methods to improve the PCE and stability of p-i-n PVSCs with a modified ETL. The modified ETL is made from depositing ntype metal oxide on top of the PCBM layer. Many metal oxides such as TiO_2 , ¹⁹⁻²¹ TiNbO, ²² ZnO, ^{23,24} Al-doped ZnO (AZO), ²⁵ SnO₂, ^{26,27} and CeO₂²⁸ have been reported, as shown in Table S1. The metal oxide ETL can withstand high temperature and humidity; thus, the stability of the cell is improved. However, the PCEs of these p-i-n planar PVSCs are relatively low and the process is complicated, especially for using sol $-gel^{21,22}$ and atomic layer deposition^{20,23,26} to prepare metal oxide films. Thus, a stable liquid suspension of metal oxide nanoparticles (NPs) is desirable for the ease of fabrication. The main issues of solution-processable metal oxide NPs are the dispersibility and the choice of solvent. A suitable solvent should be capable of dispersing NPs well and should not damage the underlying layers of PCBM and perovskite. The well-dispersed NP solution can form a smooth and dense film on top of the PCBM layer, which can provide a good interfacial contact between PCBM and the top electrode. However, the NPs tend to aggregate together to minimize the surface energy, which reduces the dispersibility and utility of them. In order to improve the dispersibility of NPs, organic molecules are usually used to modify the surface of NPs. For example, oleic acid (OA) is the most commonly used ligand for dispersing NPs. The long alkyl chain of OA can sterically hinder the aggregation of NPs, leading to well-dispersed NPs in organic solvents.^{29,30} However, molecules with long alkyl chains have a striking drawback of inhibiting the charge transport, which results in poor devices performance.³¹⁻³³

Besides the dispersibility of n-type metal oxide NPs, the band alignment is also very important for high-efficiency and stable PVSCs. The Ohmic contact is required for the interface between the semiconductor and electrode to extract charges efficiently. Generally, a low-work-function electrode such as Ca, Al, and Mg must be employed with an n-type semiconductor.³⁴ However, the low-work-function electrode is chemically reactive and easily oxidized that affects the longterm stability of PVSCs. Organic low-work-function modifiers (WFMs) have been used to lower the work function of a stable high-work-function electrode, like Ag and Au. These are, for instance, polyethylenimine (PEI),³⁵ ethoxylated polyethyleneimine (PEIE),³⁵ poly[(9,9-bis(3-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene) (PFN),³⁶ and bathocuproine (BCP).³⁷ These organic low WFMs, which usually contain ionic or polar groups of amino, quaternary ammonium salt, and phosphonate,³⁸ can create a strong molecular dipoleinduced electrical field to shift the vacuum energy level and thus lower the work function of the electrode. Therefore, the organic molecule capped on the surface of metal oxide NPs should contain molecule-induced surface dipoles to facilitate the band alignment of PVSCs and result in a good device performance. Recently, Fang et al. exchanged the OA capped on the surface of a CeO_2 nanocrystal with the short and hydrophilic acetylacetone.²⁸ Acetylacetone functions as a steric barrier to aid in the well dispersion of nanoparticles in

methanol and form a bilayer ETL on PCBM for p-i-n PVSCs. However, the investigation on the chemical structure effects of organic molecules capped on metal oxide NPs on the device performance is limited in the literature. Hence, the design of an appropriate ligand is quite a challenge.

In this study, we prepared novel dual function organicmolecule-capped metal oxide NPs with low-work-function tunability and excellent dispersibility. This new material has never been reported in the literature according to the best of our knowledge. We chose SnO₂ NPs due to their excellent conductivity, wide band gap, and chemical stability.^{39,40} Highly crystalline SnO₂ NPs with a particle size of approximately 6.4 nm were first synthesized by the solvothermal method. 41,42 The as-synthesized SnO_2 (as- SnO_2) NPs are easily aggregated and cannot form a well-dispersed suspension in either polar or nonpolar solvents. We systematically selected the suitable organic molecules to modify the metal oxide NPs and successfully developed a general ligand exchange method to disperse metal oxide NPs well in solvent. The as-SnO₂ NPs were first modified with a hydrophobic ligand, oleic acid (OA), to form OA-capped SnO₂ NPs (OA-SnO₂). The OA-SnO₂ NPs can be well-dispersed in a nonpolar solvent, such as chlorobenzene or chloroform. However, the nonpolar solvent used in the OA-capped SnO₂ suspension damaged the PCBM layer and the insulating OA hindered the extraction and transport of charges of the ETL. Therefore, we further developed a ligand exchange method using tetrabutylammonium hydroxide (TBAOH) to replace the insulating OA molecules on the surface of the SnO₂ NPs. Via the surface modification, the TBAOH-capped SnO₂ NPs can be very well dispersed in ethanol. Notably, TBAOH not only enhances the SnO₂ NP dispersion but also facilitates band alignment between SnO₂ and Ag. The TBAOH ligand forms a molecular dipole-induced electrical field at the SnO₂/Ag interface, and the electrical field makes the work function (WF) of Ag change from -4.62 to -3.99 eV. The shift of the WF dramatically reduces the contact barriers between SnO₂ and Ag, enabling the formation of Ohmic contact at the interface. The device structure of FTO/NiO_r/perovskite/PCBM/metal oxide NPs/ Ag was employed in this study. The TBAOH-capped SnO₂ NPs can form a dense and high-quality SnO₂ film on top of PCBM. By inserting a TBAOH-SnO₂ layer between PCBM and Ag, the PCE of the p-i-n PVSC greatly increases from 14.91 to 18.77%. Moreover, the thermal stability of PVSCs significantly improves by adopting the TBAOH-SnO₂ layer. We also modified various metal oxide NPs, including TiO₂, ITO, and CeO₂, using the TBAOH ligand to demonstrate the broad applicability of our method. With these modified metal oxide NPs, all of the p-i-n PVSCs exhibit remarkable improvement in device performance.

RESULTS AND DISCUSSION

The solvothermal method has been used extensively to synthesize highly crystalline metal oxide NPs. In this study, we first synthesize highly crystalline SnO_2 NPs by the solvothermal method in an autoclave under high-pressure and high-temperature conditions. The clear lattice fringe of SnO_2 NPs is observed in the images of high-resolution transmission electron microscopy (TEM) (Figure 1a,b), which indicates the formation of highly crystalline SnO_2 NPs. The (110) plane of rutile SnO_2 with a *d*-spacing of 0.33 nm was indexed (Figure 1b). The average SnO_2 particle size is 6.48 nm, which is calculated from the particle size distribution in



Figure 1. Characteristics of tin oxide nanoparticles shown in the (a) TEM image, (b) high-resolution TEM image, (c) particle size distribution, and (d) XRD spectrum.

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Figure 1c The crystallinity and purity of as-synthesized SnO₂ NPs (as-SnO₂) are further confirmed by X-ray diffraction (XRD) with sharp diffraction patterns. Figure 1d shows the characteristic peaks of as-SnO₂ NPs at 26.5, 33.9, 38.3, 51.5, and 65.5°, corresponding to the (110), (101), (200), (211), and (301) planes, respectively. We further elucidate the purity and composition of as-SnO2 NPs by X-ray photoelectron spectroscopy (XPS) analysis. Figure S1a reveals only Sn and O elements without any impurity in the XPS spectrum of as-SnO₂ NPs. In Figure S1b, two peaks at binding energies of 497.77 and 486.33 eV are assigned to Sn $3d_{3/2}$ and Sn $3d_{5/2}$ respectively. The Sn 3d peaks with symmetrical shapes and small full width at half-maximum (FWHM) show that Sn⁴⁺ is predominantly present in the as-SnO2. The XPS spectrum of O 1s (Figure S1c) can be convoluted into two peaks positioned at 530.1 and 531.1 eV, which are related to lattice oxygen and vacancy oxygen, respectively. The atomic ratio of Sn and O (Sn $3d_{5/2}$ to lattice O) is determined to be 1.00:1.75, which is less than 1.00:2.00, indicating oxygen deficiency in the as-SnO₂ NPs. The oxygen deficiency, mainly caused by the formation of oxygen vacancy, leads to an n-type characteristic of the SnO₂



Figure 2. (a) Chemical structures of OA, TBAOH, and TMAOH. (b) UPS spectra and (c) calculated work functions of Ag and OA-, TBAOH-, and TMAOH-coated Ag. (d) Energy band diagram of PVSCs fabricated using PCBM/TBAOH and schematic diagram of dipole-moment-induced vacuum level shifting. (e) *J*–*V* curves of PVSCs fabricated using PCBM, PCBM/OA, PCBM/TMAOH, and PCBM/TBAOH.

NPs. In addition, we evaluated the band structure of as-SnO₂ NPs using UV–vis spectroscopy and ultraviolet photoemission spectroscopy (UPS). An optical band gap of 3.35 eV can be calculated by the Tauc plot shown in Figure S2a. The work function (WF) and valence band of as-SnO₂ NPs are determined to be -4.80 and -7.91 eV, respectively, from the UPS spectrum (Figure S2b). Therefore, a conduction band of -4.56 eV can be obtained, which is consistent with literature data.²⁷

The uniform and dense SnO₂ film is required to obtain highefficiency solar cells. Although highly crystalline SnO₂ NPs can be synthesized, a rough and porous film usually results from strong aggregation of these NPs in either polar (methanol, ethanol) or nonpolar solvent (chlorobenzene, toluene). The well-dispersed SnO₂ NP solution is imperative to obtain a high-quality SnO₂ film. In order to improve the dispersibility of SnO₂ NPs in organic solvent, the particles should be capped with an organic molecule, which imposes steric hindrance to prevent aggregation. The size of the molecule is critical to determine the dispersibility of SnO2 NPs. It is also desirable that the organic molecule can act as a work function modifier, which provides a strong molecular dipole and lowers the work function of the electrode. The quaternary ammonium salt has shown to be a work function modifier because of its strong molecular dipole.^{43,44} Here, we propose using tetraalkylammonium hydroxide to exchange with the oleic acid (OA) ligand and to aid in the dispersion of SnO₂ NPs in alcohol. Two tetraalkylammonium hydroxides, tetramethylammonium hydroxide (TMAOH) and tetrabutylammonium hydroxide (TBAOH), were evaluated. Their structures are shown in Figure 2a. The calculated molecular volumes and dipole moments of different organic molecules are summarized in Table 1. The surfactant capabilities of OA and TBAOH are

Table 1. Calculated Molar Volumes and Dipole Moments of OA, TBAOH, and TMAOH from Gaussian Modeling Software

| organic molecule | molar volume (bohr ³ /mol) | dipole moment (debye) |
|--|--|--------------------------|
| oleic acid (OA) | 2801.98 | 1.93 |
| tetrabutylammonium hydroxide (TBAOH) | 2984.72 | 7.56 |
| tetramethylammonium hydroxide (TMAOH) | 801.71 | 7.95 |

better than that of TMAOH due to their larger molecular volumes. On the other hand, the capabilities of work function modifiers TMAOH and TBAOH are more suitable than that of OA due to their larger dipole moments. Consequently, we select tetrabutylammonium hydroxide as the capping molecule for SnO_2 NPs, which can function as a surfactant and work function modifier simultaneously.

To prove the work function tunability of tetralkylammonium hydroxide, we investigated the effect of different organic molecules on the WF of a Ag electrode using ultraviolet photoemission spectroscopy (UPS). Figure 2b,c illustrates the UPS spectra and calculated WFs, respectively. The calculated WFs of Ag, Ag/TBAOH, Ag/TMAOH, and Ag/OA are -4.62, -3.99, -4.10, and -4.39 eV, respectively. The reduced WF of Ag is attributed to the effect of molecular dipole-induced vacuum level shifting. Figure 2d shows that the LUMO of PCBM (-4.20 eV) is lower than the WF of Ag (-4.62 eV), resulting in the formation of a Schottky barrier between PCBM and Ag. The Schottky contact leads to charge accumulation at the PCBM/Ag interface.³⁷ Generally, an s-shaped J-V curve or so-called kink is observed by this interfacial charge accumulation, unbalanced charge transportation, and the Schottky barrier at the ETL/electrode interface.45 The presence of the s-shaped kink significantly reduces the fill factor, which is detrimental to the device performance. Figure 2e illustrates the effect of different organic molecules on the PCEs of PVSCs. The Schottky barrier between PCBM and Ag causes charge accumulation and recombination; therefore, the PVSCs fabricated using PCBM/Ag exhibit slight s-shaped J-Vcurves and relatively low J_{sc} (18.75 mA/cm²) and FF (74.5%) values. However, the decreasing WF of Ag can change the interfacial interaction at PCBM/Ag from the Schottky barrier to an Ohmic contact. The energy band diagram is depicted in Figure 2d. The J-V curves are changed from s-shaped to normal diode curves. The PCE of PVSCs significantly increases from 14.91 to over 16.53% after depositing either a TMAOH or TBAOH layer on top of PCBM. The results reveal the WF tunability of TMAOH and TBAOH. On the other hand, OA has a long and insulating hydrocarbon chain, making the interface highly resistive. Therefore, the PCE of the device decreases to 7.01% using OA.

To improve the dispersibility of as-SnO₂, we developed a ligand exchange method, which is shown in Figure 3a. The surface of as-SnO₂ was first modified with OA, and the chloride anion on the surface was replaced by a carboxylate anion, resulting in a stable suspension solution of OA-SnO₂ NPs in chloroform. Then, we added the stripping agent BF₃-OEt₂ into the OA-SnO₂ suspension to remove the OA ligands.⁴ After the removal of OA, the surface of SnO2 NPs was protonated and stabilized by a BF₄⁻ counter ion and the SnO₂ NPs were precipitated immediately, indicating that the OA ligands were successfully desorbed (desorbed-SnO₂). The BF₄⁻ counter ion was subsequently replaced with a short-polar ligand of tetrabutylammonium hydroxide (TBAOH) because the OH⁻ anion of TBAOH has a higher affinity for protonated- SnO_2 NPs.⁴⁷ The coordination of the OH⁻ anion with the surface makes SnO₂ NPs hydrophilic, so TBAOH-SnO₂ NPs can be completely dispersed in ethanol. We verified the process of ligand exchange by FTIR spectroscopy, as shown in Figure 3b. The characteristic peaks of as-SnO₂ NPs are located at 540–660 cm^{-1} , indicating the stretching vibrations of the O– Sn-O and Sn-O bonds.⁴⁸ In comparison to as-SnO₂, the characteristic peaks of OA-SnO₂ appear at 2800-3000, 1701, and 1400–1550 cm⁻¹, corresponding to the C-H, C=O, and COO⁻ stretching vibrations of OA molecules, respectively. After the stripping procedure, the obtained desorbed-SnO₂ shows almost undetectable OA peaks with the appearance of a new BF_4^- peak of 1042 cm⁻¹.⁴⁹ After the TBAOH ligand was capped on the SnO₂ NPs, the characteristic peaks of \bar{C} -H and O-H stretching vibrations of the TBAOH ligand appear instead of the signal of BF_4^- in FTIR (Figure 3b). Figure 3c illustrates the dispersibility of various SnO2 NPs in different solvents. The ethanol suspension of as-SnO₂ was turbid due to its low dispersibility. The chloroform suspension of OA-SnO₂ NPs was transparent due to the presence of OA as the surfactant. Upon removal of OA using BF3-OEt2, the desorbed-SnO₂ NPs were formed and precipitated. Finally, TBAOH was exchanged with BF₄⁻ to form a transparent TBAOH-SnO₂ suspension in ethanol. It is worth noting that if we skip the modification process of OA, the as- SnO_2 cannot be dispersed well in TBAOH solution. The surface of as-SnO₂

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Figure 3. (a) Schematic illustration of the ligand exchange procedure for TBAOH-capped SnO_2 nanoparticles. (b) FTIR spectra of SnO_2 nanoparticles with different treatments during the ligand exchange procedure. (c) Photos of different suspensions of SnO_2 nanoparticles.



Figure 4. (a) Device structure and (b) cross-sectional SEM image of PVSCs fabricated using the PCBM/TBAOH–SnO₂ ETL. (c) *J*–*V* curves of PVSCs fabricated using different ETLs: PCBM, PCBM/as-SnO₂, PCBM/OA–SnO₂, PCBM/TMAOH–SnO₂, and PCBM/TBAOH–SnO₂. (d) PCE distribution of PVSCs fabricated using PCBM and PCBM/TBAOH–SnO₂. The data are obtained from 25 devices of every ETL.

NPs contains hydrogen chloride,⁵⁰ which reacts directly with basic TBAOH to form TBACl and H₂O by-products (formula S1). TBACl cannot help the dispersion of SnO_2 NPs in ethanol, as shown in Figure S3. As a result, the OA modification process is necessary for our ligand exchange method. Furthermore, we let all the suspensions set for 5 h to determine their stability. After 5 h, the suspensions of as-SnO₂ and desorbed-SnO₂ show clear precipitation at the bottom, but the suspensions of OA–SnO₂ and TBAOH–SnO₂ remain stable and transparent. The improved dispersibility was further studied by dynamic light scattering measurement (DLS) (Figure S4). The as-SnO₂ NPs show a mean cluster size over 100 nm; however, the mean cluster sizes of OA–SnO₂ and TBAOH–SnO₂ are significantly smaller, at 27 and 18 nm, respectively. The result again confirmed that the TBAOH molecule is an effective surfactant to reduce the aggregation of SnO₂ NPs. To prove the structure of organic-molecule-capped metal oxide nanoparticles further, transmission electron

| | | 2 | | |
|---------------------------------|------------------------|----------------------------|--------------------------|----------------------------|
| sample | V _{oc} (V) | $J_{sc} (mA cm^{-2})$ | FF (%) | PCE (%) |
| PCBM/Ag | $1.06 (1.05 \pm 0.01)$ | $18.75 \ (18.34 \pm 0.73)$ | 74.69 (70.17 \pm 2.22) | 14.91 (13.47 \pm 0.95) |
| PCBM/as-SnO ₂ /Ag | $0.81~(0.86\pm0.03)$ | $15.65 (12.47 \pm 3.32)$ | $28.15 (23.06 \pm 4.38)$ | $3.57 (2.52 \pm 0.96)$ |
| PCBM/OA-SnO ₂ /Ag | $0.85~(0.85~\pm~0.02)$ | $21.04 \ (20.01 \pm 0.65)$ | $51.10 (41.36 \pm 9.07)$ | $9.17 (7.03 \pm 1.61)$ |
| PCBM/TMAOH-SnO ₂ /Ag | $1.06 (1.06 \pm 0.01)$ | $19.51 \ (18.72 \pm 0.46)$ | $75.70(74.53 \pm 2.35)$ | $15.66 (14.85 \pm 0.57)$ |
| PCBM/TBAOH-SnO ₂ /Ag | $1.08 (1.08 \pm 0.02)$ | $21.62 \ (20.43 \pm 0.85)$ | $80.50 (77.73 \pm 2.35)$ | $18.77 \ (17.14 \pm 0.70)$ |

Table 2. Device Characteristics of PVSCs Fabricated Using Different ETLs: PCBM, PCBM/as-SnO₂, PCBM/OA-SnO₂, PCBM/TMAOH-SnO₂, and PCBM/TBAOH-SnO₂^a

^{*a*}The average data in brackets are obtained from at least 25 devices.

microscopy-energy dispersive spectrometry (TEM-EDS) was conducted. Figure S5a shows the TEM image of the as-SnO₂ NPs. The as- SnO_2 NPs are severely aggregated, some of which even overlay on top of each other. Figure S5b shows the TEM image of TBAOH-SnO₂ NPs. The presence of TBAOH ligands clearly lets the SnO₂ NPs stay separated. This result indicates that the surface of SnO₂ NPs is indeed capped by the TBAOH ligands. In addition, we used EDS to identify further the surface chemistry of SnO₂ NPs. The EDS spectra of assynthesized SnO₂ NPs and TBAOH-SnO₂ are shown in Figure S5c,d, respectively. The as-synthesized SnO₂ NPs exhibit the EDS signals of Sn, O, and weak C. However, TBAOH-SnO₂ shows the EDS signals of Sn, O, and strong C and N. The overlapped C and N signals are from the TBAOH ligand. These results clearly reconfirm that the SnO₂ nanoparticles are capped by TBAOH. For the purpose of comparison, the tetramethylammonium hydroxide capped SnO₂ NPs (TMAOH-SnO₂) were also prepared by the same ligand exchange procedure. Figure S6 shows the poor dispersibility of TMAOH-SnO₂, compared with OA-SnO₂ and TBAOH-SnO₂. The low dispersibility of TMAOH-SnO₂ is due to the small molecular volume of TMAOH, which cannot effectively separate the SnO₂ NPs and avoid the aggregation. These results are in agreement with the modeling shown in Table 1.

To demonstrate the feasibility of the various SnO₂ layers as the ETL, we fabricated planar p-i-n PVSCs with the ETL of PCBM, composite ETL of PCBM/as-SnO2, PCBM/OA-SnO₂, PCBM/TBAOH-SnO₂, and PCBM/TMAOH-SnO₂. Figure 4a,b shows a device with the configuration of glass/ FTO/NiO_x/MAPbI₃/PCBM/TBAOH-SnO₂/Ag and its cross-sectional SEM image, respectively. The thickness of each layer of the device is 60 nm NiO_x (HTL), 375 nm MAPbI₃ (photoactive layer), and 80/40 nm PC₆₁BM/ TBAOH-SnO₂ (ETL). The J-V curves of the PVSCs with various ETLs are shown in Figure 4c, and the corresponding photovoltaic characterizations are summarized in Table 2. The PCE of PVSCs fabricated using PCBM ETL is 14.91%, with a $V_{\rm oc}$ of 1.06 V, $J_{\rm sc}$ of 18.75 mA cm⁻², and FF of 74.69%. Figure S7 shows the morphologies of the various ETLs using scanning electron microscopy (SEM). The SEM image of the pristine PCBM layer (Figure S7a) presents uniform and smooth morphology. However, for the PCBM/as-SnO₂ ETL, the poor dispersion of SnO₂ NPs in ethanol leads to rough films and discontinuous aggregates on top of the PCBM (Figure S7b). The PVSC with the PCBM ETL exhibits a slightly s-shaped J-V curve because of the formation of the Schottky barrier between the PCBM and Ag electrode. When the as-SnO₂ NPs were deposited on top of PCBM, the device shows a pronounced s-shaped kink in the J-V curve with a large reduction in FF (28.15%) and PCE (3.57%). The severe s-kink results from the poor interfacial contact between as-SnO₂ and

Ag. OA-SnO₂ and TBAOH-SnO₂ were deposited on top of the PCBM layer, and the PCEs of these PVSCs were 7.9 and 18.77%, respectively. Figure S7c shows that the film morphology of the OA-SnO₂ film is better than that of the as-SnO₂ film, and therefore, the PCE of a device with a PCBM/OA-SnO₂ ETL is better than the one with a PCBM/ as-SnO₂ ETL. However, the J-V curve of PVSC with PCBM/ OA-SnO₂ still has an s-shaped kink. The PCE of PVSC fabricated using a PCBM/TBAOH-SnO₂ ETL is surprisingly enhanced to 18.77%, with a $V_{\rm oc}$ of 1.08 V, $J_{\rm sc}$ of 21.62 mA cm^{-2} , and FF of 80.50%. It is a more than 20% improvement in PCE compared with the device fabricated using the pristine PCBM ETL. Although the OA-SnO₂ and TBAOH-SnO₂ NPs reveal comparable dispersibility, only the devices with the TBAOH-SnO₂ ETL improve the PCE. This result implies that there are other factors affecting the PCE in addition to the smooth film obtained from well-dispersed NP suspensions. We speculate that it is due to the poor conductivity of $OA-SnO_2$. The devices with a configuration of FTO/OA-SnO2 or TBAOH-SnO₂/Ag were fabricated to measure the conductivity of each layer. The conductivity is calculated from the *I*-*V* curve of the device using the equation $\sigma_0 = Id/AV$, where σ_0 is the conductivity, *I* is the current recorded under the applied voltage (V), A is the sample area (0.09 cm^2), and d is the film thickness (40 nm). The results are shown in Figure S8a,b. The conductivity of the TBAOH–SnO₂ layer (2.64 \times 10^{-6} S cm⁻¹) is 3 times higher than that of OA-SnO₂ (8.65 × 10^{-7} S cm⁻¹). In addition, we measured the mobility of TBAOH-SnO₂ and OA-SnO₂. The electron-only devices with the structure of FTO/TBAOH-SnO2 or OA-SnO2/ perovskite/PCBM/Ag were used for measurements. The results are calculated by the space charge limited current (SCLC) model and shown in Figure S8c,d. The electron mobilities of the TBAOH-SnO₂ and OA-SnO₂ films are 7.36 \times 10⁻³ and 5.63 \times 10⁻³ cm² V⁻¹ s⁻¹, respectively. As the long alkyl chain of the insulating OA molecule is exchanged with the short-chain and polar TBAOH molecules, the conductivity and mobility of TBAOH-SnO2 are greatly increased. The smooth and dense morphology of the TBAOH-SnO₂ ETL is also observed in Figure S7d, which is due to the use of the well-dispersed TBAOH-SnO₂ suspension to place the film on top of the PCBM layer. The uniformity of the TBAOH-SnO₂ film was proven by EDS mapping as shown in Figure S9. The complete Sn and O signals indicate that the TBAOH-SnO₂ film is very uniform and densely covers the entire PCBM layer. Figure S7e shows that the film of PCBM/TMAOH-SnO₂ NPs is not as smooth as that of PCBM/TBAOH-SnO₂ NPs, which causes the PCE of PVSCs to be lower (15.63%). Though the WF tunability of TMAOH is similar to that of TBAOH, the smaller molecular volume of TMAOH makes it not as good as a surfactant such as TBAOH. Moreover, we determined the variation of PCE in the PVSCs with and without TBAOH-



Figure 5. (a) Steady-state PL spectra and (b) TRPL spectra of $MAPbI_3$ deposited on the FTO/NiO_x substrate, further covered by PCBM and PCBM/TBAOH–SnO₂, respectively. *C–V* characteristics of PVSCs under varied light intensities from dark to 1 sun for devices fabricated using different ETLs of (c) PCBM and (d) PCBM/TBAOH–SnO₂. Illustration of the energy band diagram of PVSCs for devices fabricated using different ETLs of (e) PCBM and (f) PCBM/TBAOH–SnO₂.

SnO₂, as shown in Figure 4d. The data are obtained from 25 devices. The result shows that the PVSC fabricated using PCBM/TBAOH-SnO₂ is highly repeatable with small variation. To quantify the coverage amount of TBAOH on the surface of SnO₂ NPs, we conducted thermal gravimetric analysis (TGA) to calculate the amount of ligand (ligand per area) of TBAOH-SnO₂, as shown in Figure S10a. The coverage amount of TBAOH was controlled by adjusting TBAOH in ethanol at three concentrations of 7.5, 15, and 30 mg m L^{-1} . The TGA results indicate the amounts of TBAOH ligand on the SnO₂ NPs at those three concentrations to be 0.706, 0.806, and 0.925 ligand nm^{-2} , respectively. The effect of surface coverage of organic molecules on the NPs toward the device performance is shown in Figure S10b. The device performance is improved with increasing coverage amount of TBAOH on the surface of SnO₂ NPs. This result indicates that

a sufficient amount of TBAOH must be capped on the surface of SnO₂ NPs to efficiently reduce the work function of Ag and form an Ohmic contact at the TBAOH-SnO₂/Ag interface. In order to have good performance of the metal oxide ETL, the metal oxide nanoparticles should have adequate size for ease of dispersion in solvent and good film quality and high crystallinity for good properties of mobility and conductivity. We found that the SnO_2 NPs with a 2 h reaction time (2 h SnO_2) exhibit a particle size of 2.98 nm and low crystallinity while the SnO_2 NPs with a 12 h reaction time (12 h SnO_2) have a particle size of 8.06 nm and high crystallinity (Figure S11a). The size and crystallinity of the NPs will increase with increasing reaction time, and it is called the ripening effect.⁵¹ We aimed the metal oxide NPs with high crystallinity and good dispersibility. As shown in Figure S11b, the PVSC fabricated from TBAOH-12 h SnO₂ shows a better performance than

that of fabricated from TBAOH-2 h SnO₂. The better performance of PVSCs fabricated from TBAOH-12 h SnO₂ might result from the good crystallinity of 12 h SnO₂ NPs. Although the increase of crystallinity will increase the performance, the storage stability of the nanoparticle dispersion solution will decrease with increasing particle size due to the gravity effect. Thus, the 12 h SnO₂ NPs were used throughout this study.

We further optimize the film thickness of the TBAOH- SnO_2 layer by tuning the spin rate of the coating process. The J-V curves of PVSCs fabricated using PCBM/TBAOH-SnO₂ with different TBAOH-SnO2 film thicknesses are shown in Figure S12a, and the related photovoltaic characterizations are summarized in Table S2. The optimized thickness of the TBAOH-SnO₂ film is approximately 40 nm, and the PCE of the devices reaches 18.77%. As the film thickness of TBAOH- SnO_2 gradually increases, both J_{sc} and FF of the PVSCs decrease. The reduction in J_{sc} and FF results from the increasing charge accumulation and recombination owing to the extended charge transport path with the thicker film. With the TBAOH-SnO₂ layer of 95 nm, the PCE of the PSVCs deceases to 15.25% with a $V_{\rm oc}$ of 1.04 V, $J_{\rm sc}$ of 20.51 mA cm⁻² and FF of 71.52. It is interesting to observe that even though the thickness of TBAOH-SnO₂ is doubled, the PVSCs retain an acceptable PCE over 15%, which indicates sufficient tolerance to the film thickness of TBAOH-SnO₂. This result is attributed to the high crystallinity and high conductivity of TBAOH-SnO₂ NPs. Noticeably, the tolerance of TBAOH-SnO₂ film thickness provides one with a large process window, which is beneficial to large-scale mass production of devices, using the process such as slot-die coating or blade coating. We also measured the J-V characteristics of the PVSCs fabricated using PCBM and PCBM/TBAOH-SnO2 in the forward and reverse scanning directions, and the devices present a negligible hysteresis behavior (Figure S12b,c). With negligible hysteresis, the steady-state J_{sc} and PCE measured at a V_{mpp} of 0.92 V are approximately 19.5 mA cm⁻² and 17.85% (Figure S12d), respectively. Figure S13 shows the external quantum efficiency (EQE) measurements of the devices using the ETLs of PCBM and PCBM/TBAOH-SnO₂. The device with the PCBM/TBAOH-SnO₂ ETL exhibits improved EQE from 400 to 800 nm. The improving EQE implies that the interfacial charge transport becomes more effective. The integrated current densities from the EQE spectra for the PVSCs using PCBM/TBAOH-SnO2 and PCBM as ETLs are 20.40 and 18.01 mA cm⁻², respectively, which is consistent with the J_{sc} obtained from I-V measurement. These results demonstrate that the PVSCs with high PCE and reproducibility can be achieved through an additional layer of TBAOH-SnO2 deposited on the PCBM layer.

To clarify the charge transport behavior of PVSCs using the TBAOH–SnO₂ layer, we systematically investigated the interfacial interaction of PVSCs fabricated using pristine PCBM and PCBM/TBAOH–SnO₂ ETLs. Generally, the charge transport layer inserted between the perovskite layer and electrode can reduce nonradiative recombination because the built-in potential can separate the photogenerated excitons efficiently at the interface between the perovskite layer and charge transport layer. Steady-state photoluminescence (PL) was conducted to study the charge transfer behavior of MAPbI₃, MAPbI₃/PCBM, and MAPbI₃/PCBM/TBAOH–SnO₂ on FTO/NiO_x substrates, as shown in Figure 5a. From the PL results, we observed significant PL quenching when the

pristine PCBM was deposited on the top of the MAPbI₃ layer. The obvious quenching effect indicates that efficient charge transfer and reducing nonradiative recombination occur at the interface between MAPbI3 and PCBM. The PL intensity is further reduced by placing a TBAOH-SnO₂ layer on top of the PCBM layer, implying that the TBAOH-SnO₂ layer can enhance charge transport. To estimate quantitatively the dynamics of charge transfer, time-resolved photoluminescence (TRPL) measurements were performed as illustrated in Figure 5b. The exponential decay profiles were fitted by a biexponential decay model as the following equation: I(t) = $A_1 \exp(-\frac{t}{\tau_1}) + A_2 \exp(-\frac{t}{\tau_2})$, where A_1 represents the fraction of charge transfer from perovskite, τ_1 is the charge transfer lifetime, A_2 represents the fraction of charge recombination, and τ_2 is the charge recombination lifetime in the perovskite layer. The fitted PL profile contains a fast decay and a slow decay component, which, respectively, refer to the decays caused by charge transfer (τ_1) and charge recombination (τ_2) . The values of all parameters are summarized in Table 3. For

Table 3. Biexponential Fitting Results of PL Decay for Glass/FTO/NiO_x/Perovskite, Glass/FTO/NiO_x/Perovskite/PCBM, and Glass/FTO/NiO_x/Perovskite/PCBM/TBAOH–SnO₂

| sample | A_1 | $	au_1$ (ns) | A_2 | τ_2 (ns) | $\substack{	au_{	ext{average}} \\ 	ext{(ns)}}$ |
|--|-------|--------------|-------|---------------|--|
| glass/FTO/NiO _x / perovskite | 0.23 | 15.91 | 0.77 | 332.72 | 259.27 |
| glass/FTO/NiO _x / perovskite/PCBM | 1.00 | 8.60 | | | 8.60 |
| glass/FTO/NiO _x / perovskite/PCBM/ TBAOH–SnO ₂ | 1.00 | 5.43 | | | 5.43 |

the perovskite film deposited on NiO_{xy} the charge transfer lifetime (τ_1) was 15.91 ns, and the charge transfer fraction (A_1) was 23%. Upon placing either PCBM or PCBM/TBAOH- SnO_2 on top of the perovskite film, the lifetime was reduced from 15.91 to 8.6 and 5.4 ns, respectively. A smaller value of τ_1 indicates a faster charge transfer. Moreover, after the deposition of the ETL on top of perovskite, the charge transfer fraction increased from 23 to 100%, indicating that the charge transfer process dominates the decay mechanism. This means that once excitons were generated by incident light in the perovskite film, they could be completely separated by the HTL of NiOx and ETL of PCBM or PCBM/TBAOH-SnO₂.^{9,52} The average lifetime was calculated using the following equation: $\tau_{avg} = \sum_i A_i \tau_i / \sum_i A_i$. The PL lifetimes of PVSCs fabricated using PCBM and PCBM/TBAOH-SnO₂ are 8.6 and 5.4 ns, respectively. The shorter PL lifetime evidences that the charge transfer is faster; the nonradiative recombination and charge accumulation are less using the PCBM/TBAOH-SnO₂ ETL. Thus, the PCE of PVSCs is improved with the composite ETL of PCBM/TBAOH-SnO₂ as compared with the pristine ETL of PCBM.

The interfacial charge accumulation phenomenon at the ETL/Ag interface was studied by measuring C-V characteristics of the PVSCs fabricated either using PCBM/Ag or using PCBM/TBAOH-SnO₂/Ag. Figure 5c,d depicts their C-V curves. The C-V curve typically consists of three regions, including the depletion, charge accumulation, and recombination regions. Hu et al.⁵³ reported the difference of C-V

between the conventional silicon solar cell and PVSCs. They noted the anomalous C-V signal in the depletion region when the light irradiation is varied for PVSCs. The result is from the photoinduced bulk polarization in PVSCs. In addition to photoinduced bulk polarization, the shift of V_{peak} indicates how the surface accumulation of the photogenerated charges is changed with the light illumination condition. For the devices fabricated using PCBM/Ag, the first curve of C-V (from low to high value of the y-axis) has two peaks at a low voltage of 0.75 V and high voltage of 1.06 V under a dark condition. The peak located at low voltage is caused by serious charge accumulation.³⁷ On the contrary, the PVSCs fabricated using PCBM/TBAOH-SnO₂/Ag reveal only one peak, which indicates that no significant charge accumulation occurs at the TBAOH-SnO₂/Ag interface. In addition, the device with PCBM/Ag exhibits a large V_{peak} shift of 0.45 V when the illumination intensity increases from dark to 1 sun; however, the device with PCBM/TBAOH-SnO₂/Ag only shows a small V_{peak} shift of 0.07 V. The small V_{peak} shift indicates that the insertion of a TBAOH-SnO₂ layer can effectively minimize the accumulation of surface charges at the TBAOH-SnO₂/Ag interface; that is, the charge transport is more efficient at the TBAOH-SnO₂/Ag interface.^{54,55} These results are consistent with device performance as discussed before.

To confirm a reduced injection barrier at PCBM/Ag by inserting a TBAOH-SnO₂ layer, the band alignment diagram is illustrated in Figure 5e. For the devices with PCBM/Ag, the LUMO of PCBM (-4.20 eV) is lower than the WF of Ag (-4.62 eV), which leads to the formation of a Schottky barrier at the PCBM/Ag interface and thus induces the charge accumulation. However, the device using PCBM/TBAOH-SnO₂ does not reveal the charge accumulation effect, which can be attributed to the WF tunability of the TBAOH molecule capped on the surface of SnO₂. The molecular dipole of TBAOH leads to the WF of Ag to shift from -4.62 to -3.99eV. Consequently, an Ohmic contact is formed at the interface between TBAOH-SnO₂ and Ag for an efficient electron extraction as illustrated in Figure 5f. Moreover, we used Kelvin probe force microscopy (KPFM) to probe the WFs of the as-SnO₂ and TBAOH–SnO₂ films (Figure S14b). The surface potential image shows that the presence of TBAOH reduces the WF of as-SnO₂ NPs by 0.3 eV (from -4.76 to -4.46 eV), which is attributed to the TBAOH-induced dipole on the surface of SnO₂ NPs. The decreasing WF of SnO₂ films reduces the injection barrier between PCBM and SnO₂, as illustrated in Figure S14c. As a result, the charges generated from the photoexcited perovskite layer can be transferred efficiently without accumulation. These results indicate that the TBAOH ligand not only improves the dispersion of SnO₂ NPs but also facilitates the band alignment at PCBM/SnO₂ and SnO₂/Ag interfaces.

To further evaluate the broad applicability of our developed ligand exchange method, we modified various metal oxide NPs, including TiO₂, ITO, and CeO₂, using the TBAOH ligand. With the modification, all of the TBAOH-capped metal oxide NPs can be well dispersed in ethanol to form transparent stable solutions. Figure S15 shows the J-V curves of PVSCs fabricated using the various TBAOH-capped metal oxides. The s-shaped J-V curves of PVSCs can be effectively eliminated using the TBAOH-capped metal oxides. Thus, this novel procedure of ligand exchange can be applicable in most metal oxide nanoparticles.

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The perovskite layer is sensitive to humidity and heat, which makes the long-term stability of PVSCs questionable and retards the progress in commercialization. The stability of the device in humidity can be improved by an encapsulation technique, but its thermal stability issue should be resolved from the aspect of materials. One of the effective ways to improve thermal stability of PVSCs is to deposit a thermally stable metal oxide dense film onto PCBM, which can prevent the chemical component of the perovskite layer from passing through PCBM and eroding the metal electrode. Figure 6



Figure 6. Normalized PCE revolution of the devices versus aging time at different temperatures.

shows the thermal stability of PVSCs fabricated using PCBM and PCBM/TBAOH-SnO₂. These devices were encapsulated by UV curable resin and thermally aged in an oven with an increasing temperature every 20 °C from 45 to 85 °C with an increment every 240 h. Both devices maintained their initial PCEs under the aging conditions of 45 °C for 240 h. As the aging continued for another 240 h at 65 °C, the PVSCs fabricated using PCBM/TBAOH-SnO₂ still kept their PCE, but the devices fabricated using PCBM show an approximate 10% decrease in PCE. When the aging continued further for another 240 h at 85 °C, the decrease in PCE for the device with PCBM reduced to approximately 50% of initial PCE; however, the device with PCBM/TBAOH-SnO₂ only experienced an approximately 10% reduction in PCE. This result clearly indicates that the use of a TBAOH-SnO₂ layer significantly enhances the thermal stability of PVSCs. We further investigated the mechanism of thermal degradation of each layer in the device by performing depth profile analysis using time-of-flight secondary-ion mass spectrometry (ToF-SIMS). The aged samples used for the analysis were prepared at 85 °C/24 h in N_2 without encapsulation. Figure 7a shows the ToF-SIMS spectra of the PVSCs fabricated using PCBM before and after aging. After thermal aging, the depth profile reveals that the CH₃NH₃⁺ and I⁻ ions diffuse into the PCBM layer and the boundary between PCBM and MAPbI₃ becomes indistinguishable, which implies the decomposition of MAPbI₃. It is worth noting that the I^- ion signal was detected in the Ag region, which means that the I⁻ ion diffused into the PCBM layer and eroded the Ag electrode to form AgI.⁵⁶ Once the I⁻ ion reacted with Ag, the degradation reaction was accelerated from the chain reaction. This is the main reason for the performance deterioration. On the contrary, the ToF-SIMS spectrum of the PVSCs fabricated using PCBM/TBAOH-SnO₂ shown in Figure 7b did not show an evident difference before and after thermal aging. In addition to the thermal



Figure 7. ToF-SIMS depth profiles of PVSCs before and after thermal aging. The device was fabricated using different ETLs of (a) PCBM and (b) PCBM/TBAOH– SnO_2 . (c) Schematic illustration of the effect of the ETL type on the thermal degradation of PVSCs. The device fabricated using PCBM (left) and PCBM/TBAOH– SnO_2 (right).

stability, the operation stability of the PVSCs fabricated from PCBM and PCBM/TBAOH– SnO_2 was investigated. The results are presented in Figure S16. The PVSCs fabricated from PCBM/TBAOH– SnO_2 have better operation stability than the devices fabricated from pristine PCBM. These results indicate that the aforementioned ion diffusion and penetration can be effectively avoided by introducing the TBAOH– SnO_2 layer between PCBM and Ag and thus improve the thermal stability and operation stability of PVSCs. The mechanism of the thermal stability improvement is illustrated in Figure 7c.

CONCLUSIONS

In conclusion, the multiple roles are present in the performance of PVSCs when the organic-molecule-modified metal oxide NPs are used as the material of the electron transport layer in the fabrication of the device. On the one hand, the organic molecules should have a specific size to effectively separate the NPs so that the metal oxide NPs can be provided with dispersibility and processability. The good dispersibility and processability are the essential properties for a high-quality metal oxide film, which is one of the requirements for highefficiency PVSCs. On the other hand, the length of organic molecules also determines the charge transport capability, and the organic molecule with a long alkyl chain should be avoided. Moreover, the organic molecule should possess moleculeinduced surface dipoles, which can create a strong molecular dipole-induced electrical field to shift the vacuum energy level and thus facilitate the band alignment of PVSCs and result in the good device performance. As a result, we demonstrate that TBAOH is an excellent organic molecule that meets all of these requirements. We synthesized highly crystalline SnO₂ NPs (as-SnO $_2$ NPs) with a particle size of approximately 6.4 nm by the solvothermal method. The as-SnO₂ NPs easily aggregate and cannot form a well-dispersed suspension in either polar or nonpolar solvent. The dispersibility of as-SnO₂ NPs was improved using the hydrophobic ligand OA (OA-

 SnO_2), which can be readily dispersed in nonpolar solvent, such as chlorobenzene or chloroform. However, the insulating OA molecule hinders the extraction and transport of charges. In addition, the use of nonpolar solvent in the OA-SnO₂ suspension damages the PCBM layer. Thus, a facile ligand exchange method was developed using TBAOH to replace the insulating OA molecule on the surface of SnO₂ NPs. Via the surface modification, the TBAOH-SnO₂ NPs can be very well dispersed in ethanol. The TBAOH-SnO₂ NPs can form a dense and smooth high-quality SnO2 film on top of PCBM. In addition to the dispersibility improvement, the TBAOH ligand also functions as a work function modifier that optimizes the band alignment between SnO₂ and Ag. The TBAOH ligand forms an aligned dipole at the SnO₂/Ag interface, which changes the WF of Ag from -4.62 to -3.99 eV. The shift in the WF dramatically reduces the contact barriers between SnO₂ and Ag, which results in Ohmic contact formation at the interface. The PCE of the p-i-n PVSCs with the TBAOH-SnO₂ layer significantly increases from 14.91 to 18.77% as compared to the device without TBAOH-SnO₂. Moreover, the thermal stability of PVSCs is also significantly improved by adopting the TBAOH-SnO₂ layer. The methods are applicable to various metal oxide NPs, including TiO₂, ITO, and CeO₂. These TBAOH-capped metal oxide NPs can form smooth films with remarkable properties in both electron transfer and work function modification.

METHODS

Materials. Acetone (99.0%) and boron trifluoride etherate (98.0+ %, BF_3-OEt_2) were purchased from Alfa Aesar. Benzyl alcohol (99.0%), chlorobenzene (99.0+ %), chloroform (99.0+ %), dichloromethane (99.8+ %), N,N-dimethylformamide (99.8%, DMF), dimethyl sulfoxide (99.9+ %, DMSO), hexane (99+ %), isopropyl alcohol (99.8%), and toluene (99.8+ %) were purchased from Acros. Butylamine (99.5%), cerium(III) nitrate hexahydrate (99.999% Ce(NO₃)₃·6H₂O), 1,12-dodecanediol (99%), oleic acid (OA, 90%), 1-octadecene (90%), oleylamine (98%), tetramethylammonium hydroxide pentahydrate (≥97%, TMAOH), tetrabutylammonium hydroxide 30-hydrate (95+ %, TBAOH), SnCl₄, trimethylamine-Noxide dehydrate (99.999%), titanium isopropoxide (99.999%), indium acetylacetonate (99.99%, $In(acac)_3$), and tin bis(acetylacetonate)dichloride (98%, Sn(acac)₂Cl₂) were purchased from Sigma Aldrich. Diethyl ether (99.0%) and ethanol (99.99%) were purchased from Fisher Chemical. Fluorine-doped tin oxide (FTO) glasses, methylammonium iodide (MAI), lead iodide (99.9985%, PbI2), and [6,6]phenyl-C₆₁-butyric acid methyl ester (99.0%, PC₆₁BM) were purchased from Front Materials Co. Ltd.

Molecular Modeling of Organic Ligand Molecules. The molecular modeling of oleic acid (OA), tetrabutylammonium hydroxide (TBAOH), and tetramethylammonium hydroxide (TMAOH) was performed using hybrid density functional theory (DFT). Gaussian 09 software was used to carry out the calculations with the B3LYP functional and the $6-311+G^*$ basis. The geometries of these molecules were optimized in vacuum with tight convergence before the calculation of their molar volumes.

Synthesis of Oleic Acid Capped SnO₂ Nanoparticles. The SnO₂ NPs were synthesized by the solvothermal method. Typically, the precursor solution was prepared by adding 3.12 g (0.012 mol) of SnCl₄ to 20 mL of benzyl alcohol and toluene mixed solvent (3:1 by volume). Then, the precursor solution was transferred to a 25 mL Teflon-lined autoclave and heated in an oven to 180 °C for 12 h. After the reaction, the white precipitate was collected by centrifugation and washed once with diethyl ether and twice with ethanol. To prepare the OA–SnO₂ suspension, the collected SnO₂ NPs were re-dispersed in 5 mL of chloroform and excess oleic acid (OA) (1 mL) to form a milky suspension. Under ultrasonication, 1 mL of butyl amine (BA) was added to obtain a colorless transparent suspension. The OA–

 SnO_2 suspension can be purified by adding acetone to wash out excess OA and BA followed by centrifugation and re-dispersion in chloroform with a concentration of 200 mg mL⁻¹.

Synthesis of Oleic Acid Capped TiO₂ **Nanorods.** The titanium dioxide nanorods (TiO₂ NRs) were synthesized according to a literature report.⁵⁷ Typically, oleic acid (120 g) was stirred at 120 °C for 1 h in a three-neck flask under Ar flow, then cooled to 90 °C, and maintained at this temperature. Titanium isopropoxide (17 mmol) was then added into the flask. After stirring for 5 min, trimethylamine-*N*-oxide dihydrate (34 mmol) in 17 mL of water was rapidly injected. This reaction was continued for 9 h to complete hydrolysis and crystallization. Subsequently, the obtained TiO₂ NRs were washed and precipitated with ethanol to remove the residual surfactant. Finally, the TiO₂ NRs were collected by centrifugation and then redispersed in chloroform or toluene with a concentration of 200 mg mL⁻¹.

Synthesis of Oleic Acid Capped ITO Nanoparticles. The indium doped tin oxide nanoparticles (ITO NPs) were synthesized according to the literature.³⁰ A mixture of $In(acac)_3$ (100 mg, 0.24 mmol), $Sn(acac)_2Cl$) (10 mg, 0.026 mmol), oleylamine (1 mL), and octadecene (6 mL) was stirred in a three-neck flask under Ar flow and then heated to 250 °C for 30 min. After 30 min, oleic acid (0.4 mL) was injected, and the mixture was heated to 270 °C and kept for 1 h. After the mixture was cooled to room temperature, the ITO NPs were precipitated by adding 30 mL of isopropyl alcohol. The precipitated ITO NPs were collected by centrifugation and re-dispersed in 10 mL of hexane in the presence of oleylamine (0.1 mL) and oleic acid (0.1 mL). 15 mL of ethanol was added to precipitate the NPs. The ITO NPs were then collected by centrifugation and re-dispersed in toluene with a concentration of 200 mg mL⁻¹.

Synthesis of Oleic Acid Capped CeO₂ Nanoparticles. The cerium dioxide (CeO₂) nanoparticles were synthesized according to the literature.⁵⁸ Typically, 1 mmol of Ce(NO₃)₃·6H₂O (0.434 g), 2 mL of oleic acid, 2 mL of oleylamine, 4 mL of octadecene, and 2.5 mmol of 1,12-dodecanediol were added in a three-neck flask. Before starting the reaction, the solution was at first degassed at 100 °C with magnetic stirring and kept for 30 min at 100 °C under vacuum to remove water and oxygen. (Note that the degas step is necessary to prevent the explosion.) The temperature was then increased to 300 °C under Ar flow. When the temperature reached 200 °C, the solution turned turbid and brownish, indicating the nucleation of CeO₂. After a 90 min reaction time at 300 °C, the mixture was cooled to room temperature naturally and washed using acetone and ethanol. The CeO₂ NPs were finally re-dispersed in toluene with a concentration of 200 mg mL⁻¹.

Preparation of the Tetraalkylammonium Hydroxide Capped Metal Oxide NP Suspension. Two kinds of tetraalkylammonium hydroxides, tetramethylammonium hydroxide (TMAOH) and tetrabutylammonium hydroxide (TBAOH), were used to modify the metal oxide NPs or NRs. The preparation procedure is described as follows. To remove the OA molecule attached on the surface of metal oxide NPs or NRs, 50 µL of OA-metal oxide suspension was added into 3 mL of dichloromethane solution of 8 mM boron trifluoride etherate (BF3-OEt2). The metal oxide NPs or NRs were then precipitated immediately and collected by centrifugation to obtain desorbed-metal oxide NPs or NRs. To obtain the tetraalkylammonium hydroxide capped metal oxide NP or NR suspension, the desorbed-metal oxide NPs or NRs were added into the solution containing 30 mg of either TMAOH or TBAOH and 1 mL of ethanol followed by ultrasonication for a few minutes, after which the colorless suspension was obtained. The tetraalkylammonium hydroxide capped NP or NR suspension was then precipitated by adding hexane to wash out the excess tetraalkylammonium hydroxide to obtain pure tetraalkylammonium hydroxide capped metal oxide NPs or NRs. Then the precipitated metal oxide NPs or NRs were redispersed in ethanol. The TBAOH-metal oxide NP or NR suspension with a concentration of 10 mg \mbox{mL}^{-1} is a well-dispersed, stable, and clear solution, but the TMAOH-metal oxide NP or NR solution is cloudy (Figure S6).

Fabrication of the Perovskite Solar Cell. Fluorine-doped tin oxide (FTO) glasses were ultrasonically washed with acetone, methanol, and isopropanol in sequence. The HTL layer was prepared using the NiO_x NP suspension with a concentration of 20 mg mL⁻¹ in DI water, spin-coated onto cleaned FTO glasses at 2500 rpm for 60 s, and annealed at 160 °C for 30 min in air. The synthesis method of NiO_x NPs is according to the literature with some modification.⁵⁹ A 1.2 M perovskite precursor solution was prepared by mixing MAI and PbI₂ (in a 1:1 molar ratio) in 1 mL of a mixed solvent of DMF and DMSO (in a 5:2 volume ratio). Subsequently, the perovskite precursor was then spin-coated onto the as-prepared NiO_r film at 4500 rpm for 30 s in a glove box filled with nitrogen. At 15 s of the spinning process, 300 μ L of diethyl ether was dropped onto the sample to wash out the extra solvent and form a transparent intermediate perovskite phase. Then, all the samples were sequentially annealed on a hot-plate at 70 °C for 1 min and 100 °C for 2 min to form dark-brown perovskite films. Afterward, the PC₆₁BM solution (2.5 wt % in chlorobenzene) was spin-coated onto the perovskite layer at 1000 rpm for 30 s to serve as the ETL. Finally, the as-prepared TBAOH-NP or NR suspension was spin-coated onto the PC₆₁BM layer at various rotation speeds followed by 100 nm Ag electrode deposition by thermal evaporation.

Characterization of Perovskite Films and Devices. TEM images of SnO₂ NPs were obtained from an FEI transmission electron microscope (JEOL 2010F). The crystal structures of various metal oxides were determined by X-ray diffraction spectrometry (XRD) (Rigaku, TTRAXIII, Japan) using Cu K α radiation at 50 kV. The Xray photoelectron spectra (XPS) were recorded with a PHI 5000 Versa Probe system (ULVAC-PHI, Chigasaki) using a microfocused (100 μ m, 25 W) Al X-ray beam. During the measurement, the pressure of the main chamber was kept below 10^{-7} Pa by turbomolecular and ion-getter pumps. The WFs of materials were measured by ultraviolet photoelectron spectroscopy (PHI 5000 VersaProbe, ULVAC-PHI) using an ultraviolet light source of He I emission (21.2 eV, B50 W) and calculated using the equation Φ = $h\nu$ $-(E_0 - E_F)$. The UV-visible transmittance spectra were obtained using a UV-vis spectrometer (V-730, Jasco). The Fourier transform infrared spectra (FTIR) were measured by Fourier transform infrared spectroscopy (Spectrum 100, PerkinElmer). The size of nanoparticles in solution was measured by dynamic light scattering measurement (90Plus/BI-MAS). The surface morphology and height information of different ETL films were measured by scanning electron microscopy (SEM, JSM-7610FPLUS, JEOL) and atomic force microscopy (AFM, OMV-NTSC, Bruker). The J-V curves of devices were measured using a voltage source meter (Keithley 2410) under an AM 1.5 G solar simulator (Yamashita Denso YSS-50A-400A) with an irradiation of 100 mW cm⁻². Note that all of the devices were not encapsulated and all measurements were performed in air with 40% RH. The amount of ligand (ligand per area) of TBAOH-SnO was analyzed by thermal gravimetric analysis (TGA, TA Instruments Q50). The element mapping of the TBAOH-SnO₂ film was measured using an energy dispersive spectrometer (EDS, Ultim Max 170, Oxford) at 3 kV SEM acceleration voltage. The PL spectra were recorded with a continuous-wave diode laser source (PDLH-440-25, DongWoo Optron Co. Ltd.), and the emission spectra were recorded with a photomultiplier tube detector system (PDS-1, DongWoo Optron Co. Ltd.). The TRPL spectra were recorded using a time-correlated single photon counting spectrometer (WELLS-001, FX, DongWoo Optron Co. Ltd.). The pulse laser had a wavelength of 440 nm and an average power of 1 mW during operation with a excitation duration of 2 μ s. The capacitance-voltage (C-V) characteristics were recorded by electrochemical impedance spectroscopy (EIS, Solartron Analytical). Surface potential mapping was carried out by Kelvin probe force microscopy (KPFM, Digital Instruments, Nanoscope III). All time-of-flight secondary-ion mass spectrometry (ToF-SIMS) depth profiles were acquired using a PHI TRIFT V nanoToF (ULVAC-PHI, Japan) system with a dual beam sputter-and-view scheme. In the analysis phase, a pulsed C_{60}^{++} (approximately 8200 Hz, pulse length of 15 ns) rastering over a 50 $\mu m \times 50 \ \mu m$ area was applied as the primary ion. The acceleration

voltage of the incident C_{60}^{+} ion was 20 kV, and the beam current was 0.08 nA DC. For the sputter phase, a 1 kV Ar⁺ beam with a beam current of 400 nA rastered over a 1500 μ m × 1500 μ m area was utilized to remove the top surface material. These parameters were chosen to eliminate the depth profile artifacts of perovskite materials.⁶⁰

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c10717.

Additional XPS spectra, UPS spectra, DLS, photo of different suspensions, top-view SEM image, conductivity, mobility, EDS map, TGA, EQE, *J*–*V* measurements, KPFM, and operation stability (PDF)

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Notes

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REFERENCES

(1) National Renewable Energy Laboratory. *Best Research-Cell Efficiencies*. (2020). Available at https://www.nrel.gov/pv/assets/pdfs/best-research-cell-efficiencies.20200406.pdf

(2) Kim, M.; Kim, G.-H.; Lee, T. K.; Choi, I. W.; Choi, H. W.; Jo, Y.; Yoon, Y. J.; Kim, J. W.; Lee, J.; Huh, D.; Lee, H.; Kwak, S. K.; Kim, J. Y.; Kim, D. S. Methylammonium Chloride Induces Intermediate Phase Stabilization for Efficient Perovskite Solar Cells. *Joule* **2019**, *3*, 2179–2192.

(3) Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J. Surface Passivation of Perovskite Film for Efficient Solar Cells. *Nat. Photonics* **2019**, *13*, 460–466.

(4) Zheng, X.; Hou, Y.; Bao, C.; Yin, J.; Yuan, F.; Huang, Z.; Song, K.; Liu, J.; Troughton, J.; Gasparini, N.; Zhou, C.; Lin, Y.; Xue, D.-J.; Chen, B.; Johnston, A. K.; Wei, N.; Hedhili, M. N.; Wei, M.; Alsalloum, A. Y.; Maity, P.; Turedi, B.; Yang, C.; Baran, D.; Anthopoulos, T. D.; Han, Y.; Lu, Z.-H.; Mohammed, O. F.; Gao, F.; Sargent, E. H.; Bakr, O. M. Managing Grains and Interfaces via Ligand Anchoring Enables 22.3%-efficiency Inverted Perovskite Solar Cells. *Nat. Energy* **2020**, *5*, 131–140.

(5) Gu, P. Y.; Wang, N.; Wu, A.; Wang, Z.; Tian, M.; Fu, Z.; Sun, X. W.; Zhang, Q. An Azaacene Derivative as Promising Electron-Transport Layer for Inverted Perovskite Solar Cells. *Chem. – Asian J.* **2016**, *11*, 2135–2138.

(6) Said, A. A.; Xie, J.; Wang, Y.; Wang, Z.; Zhou, Y.; Zhao, K.; Gao, W. B.; Michinobu, T.; Zhang, Q. Efficient Inverted Perovskite Solar Cells by Employing N-Type (D-A1 -D-A2) Polymers as Electron Transporting Layer. *Small* **2019**, *15*, e1803339.

(7) Elbohy, H.; Bahrami, B.; Mabrouk, S.; Reza, K. M.; Gurung, A.; Pathak, R.; Liang, M.; Qiao, Q.; Zhu, K. Tuning Hole Transport Layer Using Urea for High-Performance Perovskite Solar Cells. *Adv. Funct. Mater.* **2019**, 29, 1806740.

(8) Giuri, A.; Masi, S.; Colella, S.; Kovtun, A.; Dell'Elce, S.; Treossi, E.; Liscio, A.; Esposito Corcione, C.; Rizzo, A.; Listorti, A. Cooperative Effect of GO and Glucose on PEDOT:PSS for High V_{OC} and Hysteresis-Free Solution-Processed Perovskite Solar Cells. *Adv. Funct. Mater.* **2016**, *26*, 6985–6994.

(9) Chang, C.-Y.; Wang, C.-P.; Raja, R.; Wang, L.; Tsao, C.-S.; Su, W.-F. High-efficiency Bulk Heterojunction Perovskite Solar Cell Fabricated by One-step Solution Process using Single Solvent: Synthesis and Characterization of Material and Film Formation Mechanism. J. Mater. Chem. A **2018**, *6*, 4179–4188.

(10) Yang, S.; Chen, S.; Mosconi, E.; Fang, Y.; Xiao, X.; Wang, C.; Zhou, Y.; Yu, Z.; Zhao, J.; Gao, Y.; De Angelis, F.; Huang, J. Stabilizing Halide Perovskite Surfaces for Solar Cell Operation with Wide-bandgap Lead Oxysalts. *Science* **2019**, *365*, 473–478.

(11) Wang, Q.; Bi, C.; Huang, J. Doped Hole Transport Layer for Efficiency Enhancement in Planar Heterojunction Organolead Trihalide Perovskite Solar Cells. *Nano Energy* **2015**, *15*, 275–280.

(12) Lee, P.-H.; Li, B.-T.; Lee, C.-F.; Huang, Z.-H.; Huang, Y.-C.; Su, W.-F. High-efficiency Perovskite Solar Cell using Cobalt Doped Nickel Oxide Hole Transport Layer Fabricated by NIR Process. *Sol. Energy Mater. Sol. Cells* **2020**, *208*, 110352.

(13) Chen, W.; Wu, Y.; Fan, J.; Djurišić, A. B.; Liu, F.; Tam, H. W.; Ng, A.; Surya, C.; Chan, W. K.; Wang, D.; He, Z.-B. Understanding the Doping Effect on NiO: Toward High-Performance Inverted Perovskite Solar Cells. *Adv. Energy Mater.* **2018**, *8*, 1703519.

(14) Shao, Y.; Yuan, Y.; Huang, J. Correlation of Energy Disorder and Open-circuit Voltage in Hybrid Perovskite Solar Cells. *Nat. Energy* **2016**, *1*, 15001.

(15) Shao, Y.; Xiao, Z.; Bi, C.; Yuan, Y.; Huang, J. Origin and Elimination of Photocurrent Hysteresis by Fullerene Passivation in CH₃NH₃PbI₃ Planar Heterojunction Solar Cells. *Nat. Commun.* **2014**, *5*, 5784.

(16) Zhong, Y.; Hufnagel, M.; Thelakkat, M.; Li, C.; Huettner, S. Role of PCBM in the Suppression of Hysteresis in Perovskite Solar Cells. *Adv. Funct. Mater.* **2020**, 1908920.

(17) Wang, N.; Zhao, K.; Ding, T.; Liu, W.; Ahmed, A. S.; Wang, Z.; Tian, M.; Sun, X. W.; Zhang, Q. Improving Interfacial Charge Recombination in Planar Heterojunction Perovskite Photovoltaics with Small Molecule as Electron Transport Layer. *Adv. Energy Mater.* **2017**, *7*, 1700522.

(18) Said, A. A.; Xie, J.; Zhang, Q. Recent Progress in Organic Electron Transport Materials in Inverted Perovskite Solar Cells. *Small* **2019**, *15*, e1900854.

(19) Docampo, P.; Ball, J. M.; Darwich, M.; Eperon, G. E.; Snaith, H. J. Efficient Organometal Trihalide Perovskite Planar Heterojunction Solar Cells on Flexible Polymer Substrates. *Nat. Commun.* **2013**, *4*, 2761.

(20) Kim, I. S.; Cao, D. H.; Buchholz, D. B.; Emery, J. D.; Farha, O. K.; Hupp, J. T.; Kanatzidis, M. G.; Martinson, A. B. F. Liquid Waterand Heat-Resistant Hybrid Perovskite Photovoltaics via an Inverted ALD Oxide Electron Extraction Layer Design. *Nano Lett.* **2016**, *16*, 7786–7790.

(21) Back, H.; Kim, G.; Kim, J.; Kong, J.; Kim, T. K.; Kang, H.; Kim, H.; Lee, J.; Lee, S.; Lee, K. Achieving Long-term Stable Perovskite Solar Cells via Ion Neutralization. *Energy Environ. Sci.* **2016**, *9*, 1258–1263.

(22) Chen, W.; Wu, Y.; Yue, Y.; Liu, J.; Zhang, W.; Yang, X.; Chen, H.; Bi, E.; Ashraful, I.; Grätzel, M.; Han, L. Efficient and Stable Largearea Perovskite Solar cells with Inorganic Charge Extraction Layers. *Science* **2015**, *350*, 944–948.

(23) Chang, C.-Y.; Lee, K.-T.; Huang, W.-K.; Siao, H.-Y.; Chang, Y.-C. High-Performance, Air-Stable, Low-Temperature Processed Semitransparent Perovskite Solar Cells Enabled by Atomic Layer Deposition. *Chem. Mater.* **2015**, *27*, 5122–5130.

(24) Bai, S.; Wu, Z.; Wu, X.; Jin, Y.; Zhao, N.; Chen, Z.; Mei, Q.; Wang, X.; Ye, Z.; Song, T.; Liu, R.; Lee, S.-t.; Sun, B. High Performance Planar Heterojunction Perovskite Solar Cells: Preserving Long Charge Carrier Diffusion Lengths and Interfacial Engineering. *Nano Res.* **2014**, *7*, 1749–1758.

(25) Savva, A.; Burgués-Ceballos, I.; Choulis, S. A. Improved Performance and Reliability of p-i-n Perovskite Solar Cells via Doped Metal Oxides. *Adv. Energy Mater.* **2016**, *6*, 1600285.

(26) Brinkmann, K. O.; Zhao, J.; Pourdavoud, N.; Becker, T.; Hu, T.; Olthof, S.; Meerholz, K.; Hoffmann, L.; Gahlmann, T.; Heiderhoff, R.; Oszajca, M. F.; Luechinger, N. A.; Rogalla, D.; Chen, Y.; Cheng, B.; Riedl, T. Suppressed Decomposition of Organometal Halide Perovskites by Impermeable Electron Extraction Layers in Inverted Solar Cells. *Nat. Commun.* **2017**, *8*, 13938.

(27) Zhu, Z.; Bai, Y.; Liu, X.; Chueh, C.-C.; Yang, S.; Jen, A. K.-Y. Enhanced Efficiency and Stability of Inverted Perovskite Solar Cells Using Highly Crystalline SnO₂ Nanocrystals as the Robust Electron-Transporting Layer. *Adv. Mater.* **2016**, *28*, 6478–6484.

(28) Fang, R.; Wu, S.; Chen, W.; Liu, Z.; Zhang, S.; Chen, R.; Yue, Y.; Deng, L.; Cheng, Y. B.; Han, L.; Chen, W. [6,6]-Phenyl-C₆₁-Butyric Acid Methyl Ester/Cerium Oxide Bilayer Structure as Efficient and Stable Electron Transport Layer for Inverted Perovskite Solar Cells. *ACS Nano* **2018**, *12*, 2403–2414.

(29) de Roo, J.; Justo, Y.; de Keukeleere, K.; Van den Broeck, F.; Martins, J. C.; Van Driessche, I.; Hens, Z. Carboxylic-Acid-Passivated Metal Oxide Nanocrystals: Ligand Exchange Characteristics of a New Binding Motif. *Angew. Chem., Int. Ed. Engl.* **2015**, *54*, 6488–6491.

(30) Lee, J.; Lee, S.; Li, G.; Petruska, M. A.; Paine, D. C.; Sun, S. A Facile Solution Phase Approach to Transparent and Conducting ITO Nanocrystal Assemblies. *J. Am. Chem. Soc.* **2012**, *134*, 13410–13414. (31) Lin, J.-F.; Tu, G.-Y.; Ho, C.-C.; Chang, C.-Y.; Yen, W. C.; Hsu, S.-H.; Chen, Y.-F.; Su, W.-F. Molecular Structure Effect of Pyridine-based Surface Ligand on the Performance of P3HT:TiO₂ Hybrid Solar Cell. *ACS Appl. Mater. Interfaces* **2013**, *5*, 1009–1016.

(32) Huang, Y.-C.; Hsu, J.-H.; Liao, Y.-C.; Yen, W.-C.; Li, S.-S.; Lin, S.-T.; Chen, C.-W.; Su, W.-F. Employing an Amphiphilic Interfacial

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Modifier to Enhance the Performance of a Poly(3-hexyl thiophene)/ TiO₂ Hybrid Solar Cell. J. Mater. Chem. **2011**, 21, 4450–4456.

(33) Khanzada, L. S.; Levchuk, I.; Hou, Y.; Azimi, H.; Osvet, A.; Ahmad, R.; Brandl, M.; Herre, P.; Distaso, M.; Hock, R.; Peukert, W.; Batentschuk, M.; Brabec, C. J. Effective Ligand Engineering of the $Cu_2 ZnSnS_4$ Nanocrystal Surface for Increasing Hole Transport Efficiency in Perovskite Solar Cells. *Adv. Funct. Mater.* **2016**, *26*, 8300–8306.

(34) Yue, S.; Lu, S.; Ren, K.; Liu, K.; Azam, M.; Cao, D.; Wang, Z.; Lei, Y.; Qu, S.; Wang, Z. Insights into the Influence of Work Functions of Cathodes on Efficiencies of Perovskite Solar Cells. *Small* **2017**, *13*, 1700007.

(35) Zhou, Y.; Fuentes-Hernandez, C.; Shim, J.; Meyer, J.; Giordano, A. J.; Li, H.; Winget, P.; Papadopoulos, T.; Cheun, H.; Kim, J.; Fenoll, M.; Dindar, A.; Haske, W.; Najafabadi, E.; Khan, T. M.; Sojoudi, H.; Barlow, S.; Graham, S.; Brédas, J.; Marder, S. R.; Kahn, A.; Kippelen, B. A Universal Method to Produce Low–Work Function Electrodes for Organic Electronics. *Science* **2012**, *336*, 327– 332.

(36) He, Z.; Zhong, C.; Su, S.; Xu, M.; Wu, H.; Cao, Y. Enhanced Power Conversion Efficiency in Polymer Solar Cells using an Inverted Device Structure. *Nat. Photonics* **2012**, *6*, 591–595.

(37) Chen, C.; Zhang, S.; Wu, S.; Zhang, W.; Zhu, H.; Xiong, Z.; Zhang, Y.; Chen, W. Effect of BCP Buffer Layer on Eliminating Charge Accumulation for High Performance of Inverted Perovskite Solar Cells. *RSC Adv.* **2017**, *7*, 35819–35826.

(38) Peng, X.; Hu, L.; Qin, F.; Zhou, Y.; Chu, P. K. Low Work Function Surface Modifiers for Solution-Processed Electronics: A Review. *Adv. Mater. Interfaces* **2018**, *5*, 1701404.

(39) Liang, J.; Chen, Z.; Yang, G.; Wang, H.; Ye, F.; Tao, C.; Fang, G. Achieving High Open-Circuit Voltage on Planar Perovskite Solar Cells via Chlorine-Doped Tin Oxide Electron Transport Layers. *ACS Appl. Mater. Interfaces* **2019**, *11*, 23152–23159.

(40) Jiang, E.; Ai, Y.; Yan, J.; Li, N.; Lin, L.; Wang, Z.; Shou, C.; Yan, B.; Zeng, Y.; Sheng, J.; Ye, J. Phosphate-Passivated SnO_2 Electron Transport Layer for High erformance Perovskite Solar Cells. ACS Appl. Mater. Interfaces 2019, 11, 36727–36734.

(41) Conti, T. G.; Chiquito, A. J.; Leite, E. R. Electrical Properties of SnO₂:Sb Ultrathin Films Prepared by Colloidal Deposition Process. *J. Mater. Res.* **2016**, *31*, 148–153.

(42) Ba, J.; Polleux, J.; Antonietti, M.; Niederberger, M. Nonaqueous Synthesis of Tin Oxide Nanocrystals and Their Assembly into Ordered Porous Mesostructures. *Adv. Mater.* **2005**, *17*, 2509– 2512.

(43) Lee, B. H.; Jung, I. H.; Woo, H. Y.; Shim, H.-K.; Kim, G.; Lee, K. Multi-Charged Conjugated Polyelectrolytes as a Versatile Work Function Modifier for Organic Electronic Devices. *Adv. Funct. Mater.* **2014**, *24*, 1100–1108.

(44) Li, C. Z.; Chueh, C. C.; Ding, F.; Yip, H. L.; Liang, P. W.; Li, X.; Jen, A. K. Doping of Fullerenes via Anion Induced Electron Transfer and Its Implication for Surfactant Facilitated High Performance Polymer Solar Cells. *Adv. Mater.* **2013**, *25*, 4425–4430.

(45) Zuo, L.; Yao, J.; Li, H.; Chen, H. Assessing the origin of the S-shaped I–V curve inorganic solar cells: An improved equivalent circuit model. *Sol. Energy Mater. Sol. Cells* **2014**, *122*, 88–93.

(46) Doris, S. E.; Lynch, J. J.; Li, C.; Wills, A. W.; Urban, J. J.; Helms, B. A. Mechanistic Insight into The Formation of Cationic Naked Nanocrystals Generated under Equilibrium Control. *J. Am. Chem. Soc.* **2014**, *136*, 15702–15710.

(47) Song, J. H.; Choi, H.; Pham, H. T.; Jeong, S. Energy Level Tuned Indium Arsenide Colloidal Quantum Dot Films for Efficient Photovoltaics. *Nat. Commun.* **2018**, *9*, 4267.

(48) Orel, B.; Lavrenčič-Štankgar, U.; Crnjak-Orel, Z.; Bukovec, P.; Kosec, M. Structural and FTIR Spectroscopic Studies of Gel Xerogel Oxide Transitions of SnO_2 and $SnO_2 \bullet$ Sb Powders and Dip-Coated Films Prepared via Inorganic Sol-Gel route. *J. Non-Cryst.* **1994**, *167*, 272–288.

(49) Dong, A.; Ye, X.; Chen, J.; Kang, Y.; Gordon, T.; Kikkawa, J. M.; Murray, C. B. A Generalized Ligand Exchange Strategy Enabling Sequential Surface Functionalization of Colloidal Nanocrystals. J. Am. Chem. Soc. 2011, 133, 998–1006.

(50) De Roo, J.; Van den Broeck, F.; De Keukeleere, K.; Martins, J. C.; Van Driessche, I.; Hens, Z. Unravelling the Surface Chemistry of Metal Oxide Nanocrystals, the Role of Acids and Bases. *J. Am. Chem. Soc.* **2014**, *136*, 9650–9657.

(51) Tu, Y.-C.; Lin, J.-F.; Lin, W.-C.; Liu, C.-P.; Shyue, J.-J.; Su, W.-F. Improving the Electron Mobility of TiO_2 Nanorods for Enhanced Efficiency of a Polymer–Nanoparticle Solar Cell. *CrystEngComm* **2012**, *14*, 4772–4776.

(52) Liang, P.-W.; Liao, C.-Y.; Chueh, C.-C.; Zuo, F.; Williams, S. T.; Xin, X.-K.; Lin, J.; Jen, A. K.-Y. Additive Enhanced Crystallization of Solution-Processed Perovskite for Highly Efficient Planar-Heterojunction Solar Cells. *Adv. Mater.* **2014**, *26*, 3748–3754.

(53) Wu, T.; Collins, L.; Zhang, J.; Lin, P. Y.; Ahmadi, M.; Jesse, S.; Hu, B. Photoinduced Bulk Polarization and Its Effects on Photovoltaic Actions in Perovskite Solar Cells. *ACS Nano* **2017**, *11*, 11542– 11549.

(54) Zang, H.; Hsiao, Y. C.; Hu, B. Surface Charge Accumulation Effects on Open Circuit Voltage in Organic Solar Cells Based on Photoinduced Impedance Analysis. *Phys. Chem. Chem. Phys.* **2014**, *16*, 4971–4976.

(55) Ahmadi, M.; Hsiao, Y.-C.; Wu, T.; Liu, Q.; Qin, W.; Hu, B. Effect of Photogenerated Dipoles in the Hole Transport Layer on Photovoltaic Performance of Organic-Inorganic Perovskite Solar Cells. *Adv. Energy Mater.* **2017**, *7*, 1601575.

(56) Li, J.; Dong, Q.; Li, N.; Wang, L. Direct Evidence of Ion Diffusion for the Silver-Electrode-Induced Thermal Degradation of Inverted Perovskite Solar Cells. *Adv. Energy Mater.* **2017**, *7*, 1602922. (57) Lin, Y.-T.; Zeng, T.-W.; Lai, W.-Z.; Chen, C.-W.; Lin, Y.-Y.; Chang, Y.-S.; Su, W.-F. Efficient Photoinduced Charge Transfer in TiO₂ Nanorod/Conjugated Polymer Hybrid Materials. *Nanotechnology* **2006**, *17*, 5781–5785.

(58) Deori, K.; Kalita, C.; Deka, S. (100) Surface-Exposed CeO₂ Nanocubes as An Efficient Heterogeneous Catalyst in The Tandem Oxidation of Benzyl Alcohol, Para-chlorobenzyl Alcohol and Toluene to The Corresponding Aldehydes Selectively. *J. Mater. Chem. A* **2015**, *3*, 6909–6920.

(59) Yin, X.; Chen, P.; Que, M.; Xing, Y.; Que, W.; Niu, C.; Shao, J. Highly Efficient Flexible Perovskite Solar Cells Using Solution-Derived NiOx Hole Contacts. *ACS Nano* **2016**, *10*, 3630–3636.

(60) Hou, C.-H.; Hung, S.-H.; Jhang, L.-J.; Chou, K.-J.; Hu, Y.-K.; Chou, P.-T.; Su, W.-F.; Tsai, F.-Y.; Shieh, J.; Shyue, J.-J. Validated Analysis of Component Distribution Inside Perovskite Solar Cells and Its Utility in Unveiling Factors of Device Performance and Degradation. ACS Appl. Mater. Interfaces **2020**, *12*, 22730–22740.