85 °C/85%-Stable n-i-p Perovskite Photovoltaics with NiO$_{x}$ Hole Transport Layers Promoted By Perovskite Quantum Dots

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Power conversion efficiency (PCE) and long-term stability are two vital issues for perovskite solar cells (PSCs). However, there is still a lack of suitable hole transport layers (HTLs) to endow PSCs with both high efficiency and stability. Here, NiO$_{x}$ nanoparticles are promoted as an efficient and 85 °C/85%-stable inorganic HTL for high-performance n-i-p PSCs, with the introduction of perovskite quantum dots (QDs) between perovskite and NiO$_{x}$ as systematic interfacial engineering. The QD intercalation enhances film morphology and assembly regulation of NiO$_{x}$ HTLs. Due to structure–function correlations, hole mobility within NiO$_{x}$ HTL is improved. And the hole extraction from perovskite to NiO$_{x}$ is also facilitated, resulting from reduced trap states and optimized energy level alignments. Hence, the promoted NiO$_{x}$-based n-i-p PSCs exhibit high PCE (21.59%) and excellent stability (sustaining 85 °C aging in air without encapsulation). Furthermore, encapsulated solar modules with QDs-promoted NiO$_{x}$ HTLs show impressive stability during 85 °C/85% aging test for 1000 hours. With high transparency, QDs-promoted NiO$_{x}$ is also demonstrated to be an advanced HTL for semitransparent PSCs. This work develops promising NiO$_{x}$ inorganic HTL in n-i-p PSCs for manufacturing next-generation photovoltaic devices.

1. Introduction

Perovskite solar cells (PSCs) have reached remarkable certified power conversion efficiencies (PCEs) up to 25.7% with n-i-p configuration.[1] In the n-i-p devices, p-type organic semiconductors (e.g., spiro-OMeTAD,[2] PTAA,[3] P3HT[4]) have been usually chosen as hole transport layers (HTLs) to achieve high PCEs. However, the intrinsic photothermal instability or external hydrophilic ionic doping of these organic HTLs limits their further application in commercial manufacture.[5] To solve this stability issue, adopting inorganic HTLs (io-HTLs) with great thermal stability has been considered as a promising solution.[6] Up till now, most reports of io-HTLs in n-i-p PSCs have focused on Cu-based inorganic semiconductors.[7] But the stability concerns still exist, due to the oxidation tendency of Cu(I) ions[8] and the chemical reactivity between the anions (e.g., SCN$^-$, I$^-$) and metal electrodes.[9] Furthermore, their deposition methods are not feasible for practical process, due to the inevitable toxic solvents[10] (e.g., sulfide) or uncontrollable post treatments[11] (e.g., gas–solid and solid–solid reactions). Therefore, finding a stable, processable and chemically compatible io-HTL for n-i-p devices is of great significance.

As an inorganic oxide semiconductor, p-type NiO$_{x}$ shows its advantages in efficient and stable p-i-n PSCs[12] benefitting from its high hole mobility,[13] matched energy level with perovskite[14] and good stability against moisture and heat.[15] In most cases, dense NiO$_{x}$ HTLs on FTO/ITO were prepared by pyrolysis of sol–gel precursors over 300 °C,[16] O$_2$-involved atomic layer deposition[17] or deposition of pre-synthesized aqueous NiO$_{x}$ nanoparticles (NPs).[12a,18] However, these above processes are not applicable for the deposition of NiO$_{x}$ HTLs on the perovskites in n-i-p devices. Instead, NiO$_{x}$ NPs with oleophilic ligands that can be dissolved in nonpolar solvents have been achieved in previous work for the deposition of NiO$_{x}$ on perovskite layers. But the corresponding devices showed inferior efficiencies (<16%) and unsatisfactory stabilities, due to the incompact assembly and low hole transport capability of NiO$_{x}$ NPs on perovskites.[19] Therefore, realizing uniform and ordered NiO$_{x}$
films on perovskite surface is a key point in fabricating high-performance NiO-based n-i-p devices.

In this work, we aim to find an effective strategy to improve steric arrangement of NiO NPs to form uniform and ordered NiO HTLs on perovskites. As reported, the properties of the substrate’s surface influenced the assembly behavior of nanoparticles. Therefore, we assumed that perovskite quantum dots (QDs) with long-chain oleophilic would tune the surface properties of perovskite layer and thus regulate the assembly behavior of NiO NPs. For the NiO HTLs, QD intercalation improved the film formation and regulation of NiO NPs, along with p-type properties due to structure–function correlation. For the perovskite layers, QD intercalation passivated the trap states and optimized the energy alignments of perovskite and NiO, thus accelerating the hole extraction and reducing nonradiative recombination. Through systematic interfacial engineering, the devices fabricated with QDs-promoted NiO HTLs exhibited high efficiencies and excellent stabilities. The superiority of QDs-promoted NiO HTLs was further extended to opaque large-scale perovskite solar modules and small-area semi-transparent perovskite cells, exhibiting excellent performance (survived at 85 °C/85% relative humidity (RH) for 1000 h). To our best knowledge, this is the first case using NiO HTLs in n-i-p type solar modules and semi-transparent cells with remarkable performance. This work shows great potential of QDs-promoted NiO HTLs in future commercial application of perovskite photovoltaics.

2. Results and Discussions

2.1. Steric and Electronic Improvement of NiO HTLs By QD Intercalation

After confirming the successful synthesis of oleophilic NiO NPs (Figures S1–S3, Supporting Information) and CsPb$_{1.85}$Br$_{1.15}$ QDs (Figure S4, Supporting Information), we deposited NiO HTLs by spin-coating NiO NPs on perovskites or QDs-covered perovskite films. As reported, the uniformity of NiO films on perovskites is an important factor affecting device’s performance. However, the pristine NiO film showed poor morphology when being deposited directly on perovskite. Most of the NiO NPs aggregated at the grain boundaries of perovskite, leading to nonradiative charge recombination centers and instability concerns due to direct contact between perovskite and electrode. To overcome the problem, QD intercalation was introduced to assist NiO film formation. NiO NPs could form a uniform and compact film on QDs-covered perovskite surface (Figure 1b). The QDs-promoted NiO film showed improved uniformity with decreased roughness, as tested by atomic force microscopy (AFM) and energy-dispersive X-rayspectroscopy (EDX) (Figures S5 and S6, Supporting Information). Moreover, the homogenous NiO film avoided direct contact between perovskite and Au electrode in n-i-p devices (Figure S7, Supporting Information). Besides improved film coverage, NiO NPs showed promoted self-assembly behavior with QD intercalation. From small angle X-ray scattering (SAXS) spectra of NiO films (Figure 1c), a scattering peak raised at 0.6 1/Å for the QDs-promoted NiO film, indicating the enhanced regularity of NiO domains; while no evident peak was shown for pristine NiO film. The improvement of NiO assembly behavior resulted from beneficial interaction between QDs and stearate ligands on NiO nanoparticles (Figure S8, Supporting Information).

Due to optimized steric regulation of NiO film and structure–function correlation, the electronic status of NiO HTL was altered after QD promotion. As shown in X-ray photoelectron spectroscopy (XPS) spectra, NiO films were verified to be nonstoichiometric, consisting of Ni$^{2+}$ and Ni$^{3+}$ simultaneously (Figure 1d,e). Ni$^{3+}$ ions were reported to result from holes around Ni$^{2+}$ vacancies in the lattice and generate p-type conductivity in the NiO films. This means the higher concentration of Ni$^{3+}$...
Figure 2. Surface passivation of perovskite and energy level adjustment between perovskite and NiOx with QD interlayer. a) TRPL spectra of PVK films with QDs, NiOx or both. b,c) Confocal PL intensity maps of the corresponding films. d) SCLC measurements of devices with the as-drawn structure. e) UPS spectra of corresponding films. f) Schematic of energy band alignments of perovskite and NiOx without or with QDs. The white dotted lines refer to Fermi levels and the green arrows refer to holes transportation.

2.1. QD intercalation in NiOx film

QD intercalation in NiOx film plays a crucial role in hole transport. Compared with the pristine NiOx, the QD-promoted NiOx exhibited a higher ratio of Ni3+/Ni2+ (raised from 1.38 to 1.96). QD intercalation influences binding states of stearate ligands on NiOx, altering electronic status of Ni2+/Ni3+ (Figure S8, Supporting Information). In addition, there was a noticeable reduction of hydroxyl groups in NiOx films with QD intercalation, which could be attributed to higher ligand coverage of NiOx NPs. The uniform QDs-promoted NiOx HTL with negligible -OH could protect the perovskite layer against moisture-induced degradation.

Benefiting from the optimized film morphology, improved assembly regularity and preferred p-type characteristics with QDs, the hole mobility of NiOx HTLs showed a more than threefold increase, from 3.98 × 10−5 to 1.29 × 10−4 cm2 V−1 s−1 (Figure 1f). Furthermore, the densely-packed NiOx films also resulted in hydrophobicity improvement, as approved by increased water contact angle, and prolonged water dipping time (Figures S9 and S10, Supporting Information). The unencapsulated perovskite covered with QDs-promoted NiOx film remained black even being directly dipped into water for 45 min, demonstrating outstanding stability against moisture. Therefore, schematics of NiOx films’ morphology were proposed in Figure 1g, intuitively showing that QD intercalation improved compactness of NiOx film on perovskite and increased hole extraction.

2.2. Enhancement in Hole Extraction from Perovskite to NiOx HTL By QD Intercalation

QD intercalation not only improved the hole mobility in NiOx HTLs, but also enhanced the hole extraction from PVK to NiOx, demonstrating the multiple roles of QDs in systematic interfacial engineering. As shown in Figure S11 (Supporting Information), QDs mainly assembled at the grain boundaries of perovskite crystals. With the modification of QDs, the trap state density on perovskite film decreased and the charge recombination was suppressed, as demonstrated by steady-state PL (Figure S12, Supporting Information) and time-resolved PL spectra (Figure 2a). The QDs-covered PVK film showed a longer lifetime than the pristine PVK, indicating reduced nonradiative recombination centers for photoinduced charges in the former. The PVK film with NiOx exhibited shorter carrier lifetime after QD intercalation, indicating more efficient hole transfer. PL intensity mapping (Figure 2b) also confirmed the above result, showing that the emission distribution of PVK film was more uniform after QD intercalation. Moreover, the sample with QDs-promoted NiOx HTLs displayed more uniform intensity distribution and faster PL decay than the pristine one (Figure 2c). After QD intercalation, more effective hole extraction resulted from fewer nonradiative recombination centers, indicating less trap states...
Figure 3. Performance enhancement of NiO$_x$-based PSCs with QD interlayers. a) Schematic of device configuration in this work and representative TEM images of NiO$_x$ NPs and CsPb$_{1.85}$Br$_{1.15}$ QDs. b) Cross-sectional SEM image of the PSC with QDs-promoted NiO$_x$ HTL. c) J–V curves of the best NiO$_x$-based device without or with QDs (active area: 0.12 cm$^2$). d) Storage stabilities of unencapsulated devices aged at 85 °C and 50% RH in air. e) Operational stabilities of the corresponding devices at MPP under 1-sun illumination. f) Depth profiling of ToF-SIMS for aged devices without or with QDs.

for carriers at the interface between PVK and NiO$_x$. Then, the measurement of space-charge-limited current (SCLC) was carried out to calculate the density of trap states (Figure 2d; Figure S13, Supporting Information). The trap-state density showed nearly twofold decrease after QD promotion. Due to fewer trap states on QDs-covered perovskite, the impedance for charge recombination was improved and the resistance for charge transfer was declined (Figure S14, Supporting Information). And the dark current density of the QDs-promoted device was obviously lower than that of the control device, indicating that QDs prevented current leakage within the devices (Figure S15, Supporting Information).

Besides passivation effect of QDs on perovskite films, energy level alignments between each layer are an important factor in terms of charge transfer. The Fermi levels and the highest occupied molecular orbital (HOMO) levels of perovskite and NiO$_x$ films without or with QDs were measured by UPS spectra and Kelvin-probe force microscopy (KPFM) (Figure 2e; Figure S16, Supporting Information). The energy fall between the HOMO level of PVK and HTL could result in an enormous interfacial charge recombination and a large $V_{OC}$ loss in the whole device. The HOMO level of QDs-covered perovskite layer (~5.44 eV) was higher than the pristine perovskite (~5.55 eV), while the HOMO level of QDs-promoted NiO$_x$ HTL (~5.29 eV) was lower than the pristine NiO$_x$ deposited directly on perovskite (~5.21 eV). The shrunken energy gap would facilitate hole extraction through layers (Figure 2f). The Fermi level of NiO$_x$ also shifted from ~4.52 to ~4.70 eV upon QD intercalation, showing more p-type property and thus higher hole mobility of QDs-promoted NiO$_x$. This was attributed to increased Ni$^{3+}$/Ni$^{2+}$ ratios in QDs-promoted NiO$_x$ film as discussed above. The lower HOMO energy of QDs-promoted NiO$_x$ contributed to a higher built-in potential of the whole device, as tested with the Mott–Schottky plot (Figure S17, Supporting Information). As discussed above, QD intercalation was proved to facilitate hole transfer from PVK to NiO$_x$ and thus improve device’s efficiency.

2.3. Overall Performance Boost of PSCs with QDs-Promoted NiO$_x$ HTLs

Based on the improvement in the properties of NiO$_x$ HTL and hole extraction between perovskite and NiO$_x$, QD intercalation promoted NiO$_x$ NPs as effective io-HTLs to boost the overall performance of n-i-p PSCs. The devices with structure of FTO/ZnTiO$_3$/FA$_{0.85}$MA$_{0.15}$Pb$_{1.85}$Br$_{1.15}$/QDs/NiO$_x$/Au were fabricated (Figure 3a, b). The QD interlayer was too thin to be visible in the cross-sectional scanning electron microscopy (SEM) image. Thus, cross-sectional EDX mappings (Figure S18, Supporting Information) and depth profiling of time-of-flight secondary-ion mass spectrometry (ToF-SIMS) (Figure 3f) confirmed the existence of QDs between perovskite and NiO$_x$. The independent peaks for Ni and Cs element in ToF-SIMS demonstrated separate layers of QD interlayer and NiO$_x$ HTL. The
device with pristine NiOx HTL was achieved by spin-coating 15 mg mL−1 NiOx (dispersed in mixed chloroform and chlorobenzene) on perovskite without further annealing to reach the highest efficiency (Figure S19 and Table S1, Supporting Information). Surprisingly, the device with QDs-promoted NiOx HTL exhibited a significant PCE enhancement and hysteresis reduction, with the top efficiency from 18.75% to 21.59% (Figure 3c; Table S2, Supporting Information). The reproducibility was demonstrated from the sum of 30 devices for each type, with average PCE increasing from 17.71% (without QDs) to 20.52% (with QDs) (Figure S22, Supporting Information). Also, the device with QDs-promoted NiOx HTL showed higher efficiency than other reported n-i-p devices with NiOx NPs and were even comparable to the fully developed p-i-n devices with NiOx NPs, as listed in Table S3 in the Supporting Information.

Besides efficiency improvement, the storage and operational stability of PSCs with QDs-promoted NiOx HTLs were also enhanced. The heat/damp stabilities of unencapsulated devices were tested under harsh condition at 85 °C with 50% RH in ambient air. The unencapsulated PSCs with QDs-promoted NiOx showed improved thermal and damp stability, remaining over 85% of original PCE after 400 h while the PCE of control device swiftly fell after 150 h (Figure 3d). NiOx-based devices presented much better stability than the ones with common HTL, spiro-OMeTAD (Figure S23, Supporting Information). Besides, operational stability of the devices were tracked at maximum power point (MPP). The device with QDs-promoted NiOx exhibited stable continuous output, indicating stable hole extraction therein (Figure 3e). To figure out the degradation process, 200-h-aged devices without or with QD intercalation was characterized and compared with fresh ones (Figure S24, Supporting Information). The results showed that the phase stability of perovskite in NiOx-based devices was improved by QDs. Furthermore, the suppression of upward I− migration was illustrated by ToF-SIMS (Figure 3f), due to the denser film morphology of NiOx HTL with QD intercalation. In addition, cross-sectional SEM-EDX mapping and aging test in isopropanol further confirmed the improved stability of devices with QDs-promoted NiOx HTLs (Figures S25 and S26, Supporting Information). The above results showed the advantages of QDs-promoted NiOx PSCs in terms of both PCE and stability. The universality of QDs-promoted NiOx HTLs were further verified in other perovskite systems like MAPbI3 (Figure S27 and Table S2, Supporting Information). The successful realization of QDs-promoted NiOx HTLs in n-i-p PSCs can compensate for the shortcomings of other HTLs in regular devices, as systematically analyzed in Table 1.

### 2.4. Practical Application of QDs-Promoted NiOx HTLs in Large-Area Modules and Semitransparent Devices

After demonstrating the feasibility of NiOx HTLs promoted by QDs in small-area PSCs, the application of QDs-promoted NiOx HTLs was further extended to opaque large-scale perovskite solar modules and semitransparent small solar devices, showing great potential for future commercial manufacture. QDs-promoted NiOx has been proved to form uniform and pin-hole-free films on perovskites at a scale of 36 cm² (Figure S28, Supporting Information), ready for solar module fabrication. Then 36-cm² solar modules (18-cm² aperture area) consisting of 8 separate cells in series were fabricated with NiOx HTLs (Figure 4a; Figure S29, Supporting Information). QD intercalation endowed NiOx-module with increased PCE (from 16.94% to 19.10%) (Figure 4b; Table S4, Supporting Information). The encapsulated QD-promoted NiOx-based module also exhibited improved operational and storage stability. The continuous operational stabilities of encapsulated modules were tracked at MPP output in ambient air (≈50 °C/50% RH) under 1-sun illumination. The QDs-promoted module showed significant improvement in working stabilities as compared with the control module during 1000-min tracking (Figure 4c). Furthermore, the storage stabilities of encapsulated modules under extreme condition were tested at 85 °C. 85% RH for 1000 h (Figure 4d). The module with pristine NiOx showed a rapid decay in the first 200 h, and maintained only 62% of the initial efficiency after 1000-h aging. The device with QDs-promoted NiOx showed better stability with 86% of PCE left after 1000 h, benefiting from the ordered and denser NiOx film with fewer hydroxy groups. The improvement in long-term stability of PCE with QD intercalation mainly lies in the enhanced stability of fill factor (Figure S30, Supporting Information). As far as we know, the HTLs that can resist aging at 85 °C/85% RH are rare in n-i-p devices.[23] Thus, the development of NiOx as stable io-HTL for n-i-p devices is of great significance for the manufacture of commercially viable solar modules in the future.

In addition, inspired by high transmittance of NiOx between 300 and 800 nm (light absorption range of perovskite films), QDs-promoted NiOx was extended to the fabrication of semitransparent PSCs (ST-PSCs), which have great potential in building-integrated photovoltaics and tandem cells. Sectional configuration of the ST-device was presented in Figure 5a, with transparent conducting oxide as transparent electrodes at both sides. The transmittance of NiOx was higher than spiro-OMeTAD (Figure S31, Supporting Information). After deposition of MoOx/ITO as transparent top electrode, the transmittance of NiOx film

| Table 1. Advantages (√) and disadvantages (×) of each kind of HTLs for n-i-p PSCs. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| HTLs            | PCE             | Stability       | Processability  | Electrode       |
| Organic materials | √               | ×               | ×               | ×               | √               |
| Cu-based inorganic compounds | √               | √               | √               | ×               | ×               |
| Sol-gel NiOx    | ×               | √               | √               | √               | √               |
| Aqueous NiOx NPs | ×               | √               | √               | √               | ×               |
| Previous nonaqueous NiOx NPs | ×               | √               | √               | √               | ×               |
| This work: QDs-promoted NiOx NPs | √               | √               | √               | √               | √               |
were also required. FAMAPb(IBr)3 perovskites with thickness
to ensure transmittance. To ensure trans-

cross-sectional SEM of the

The pristine NiO

Benefited from ultra-thin perovskite

Finally, the product was dispersed in hexane and left overnight. The insoluble precipitate was removed by centrifugation. NiO

SC had no more than 5% variation (Figure 5d; Table S6, Supporting Information). The QDs-promoted one had higher efficiencies illuminated from the FTO side and ITO side, respectively (Figure 5c; Table S6, Supporting Information). The QDs-promoted NiOx HTLs helped to fabricate n-i-p devices with high efficiency and distinguished stability, showing great potential in fabrication of large-scale devices and semitransparent devices. Through systematic interfacial engineering by multifunctional QDs, this work paves the way for the commercialization of n-i-p perovskite photovoltaics based on NiOx or other p-type nanoparticle HTLs.

3. Conclusion

In conclusion, NiOx-based HTLs have been successfully promoted by QD intercalation and applied in n-i-p PSCs. The QD intercalation between perovskites and NiOx was found to improve hole mobility within NiOx films by enhancing film morphology and steric regularity of NiOx films, and facilitate hole extraction from perovskites to HTLs by passivating defects and optimizing HOMO level alignments. QDs-promoted NiOx HTLs helped to fabricate n-i-p devices with high efficiency and distinguished stability, showing great potential in fabrication of large-scale devices and semitransparent devices. Through systematic interfacial engineering by multifunctional QDs, this work paves the way for the commercialization of n-i-p perovskite photovoltaics based on NiOx or other p-type nanoparticle HTLs.

4. Experimental Section

Synthesis Methods: NiOx nanoparticles were synthesized using a non-injection method as previously reported. The reaction mixture containing nickel stearate (3 mmol, Sinopharm Chemical Regent Co., Ltd.), lithium stearate (1.2 mmol, Sinopharm), 1-octadecanol (18 mmol, Alfa Aesar) and 1-octadecylamine (ODE, 30 mL, Alfa Aesar) was added to a two-neck flask under nitrogen and dissolved at 80 °C. Then the system was sealed and heated at 245 °C for 3 h. After the reaction was cooled to room temperature, the product was collected by adding a mixture of hexane (20 mL, Sinopharm) and ethyl acetate (20 mL, Sinopharm), and further purified using the combination of hexane (Sinopharm) and ethanol (Sinopharm). Finally, the product was dispersed in hexane and left overnight. The insoluble precipitate was removed by centrifugation. NiOx nanoparticles were extracted by adding ethanol to the liquid supernatant. After centrifugation, the final product was dried under vacuum.

CsPbI2Br1−x quantum dots were synthesized by the commonly-used one-pot hot-injection method. Cs2CO3 (0.4 g, Tokyo Chemical Industry Co., Ltd. (TCI)), ODE (40 mL), and oleic acid (2.5 mL, TCI) were loaded into 100 mL 3-neck flask and the mixture was dissolved under a vacuum at 120 °C for 0.5 h. Then, the flask was refilled with N2 and preheated to 70 °C. In another pot, different ratios of PbBr2 (TCI) and PbI2 (Xi'an Baolai Corp), which is defined by chemical formula of CsPbI2Br1−x, QDs, were added together with 1-octadecane (the concentration of Pb2+ was 1 M). The mixtures were degassed under a vacuum (< 0.1 Torr) at 120 °C for 1 h and excess oleic acid (10 mL) and oleylamine (10 mL, Aladdin) (both preheated at ≈ 70 °C) were injected. After PbBr2 and PbI2 were completely dissolved, the Cs-oleate compound was swiftly injected into the reaction mixture at 175 °C. After the reaction mixture was quenched by an ice bath (< 5 s after injection), methyl acetate (MeOAc, 70 mL, ultradry, Aladdin) was added into the supernatant to precipitate QDs. Then the wet pellets of QDs were washed with hexane twice and precipitated again with an equal volume MeOAc. After that, the remained solids were dried in a vacuum at room temperature to obtain QDs with uniform sizes.

Device Fabrication: 0.12-cm2 perovskite solar cell: First, ZnTiO3 (ZTO) electron transport layer was deposited on clean and patterned 2 × 2 cm2 FTO by spray coating the mixture solution of Zn(OAc)2 (2.5 mL, 0.2 m in ethanol, Sinopharm), titanium disopropoxide bis(acetylacetonate) (0.5 mL, 75% in isopropanol, Alfa Aesar), and thiourea (4.7 mg) in ethanol (50 mL) at 450 °C for 30 min, as reported in our previous work. Then, perovskite films with different compositions were deposited by spin-coating methods. A solution of 900 mg FAPbI3, 22.5 mg MAPbBr3, 65 mg PbI2, 33 mg MACI dissolved in 1 mL
Figure 5. Performance development of semi-transparent NiO$_x$-based solar devices. a) Schematic of semitransparent device with n-i-p configuration. b) Transmittance spectra and photo (inset) of the full ST-devices. c) $J$–$V$ curves of ST-devices illuminated from both sides. d) IPCE plots and integrated $J_{SC}$ for the corresponding ST-devices.

DMF/DMSO (4/1) was spun at 1200 rpm for 5 s followed by 6000 rpm for 20 s, with diethyl ether sprayed at 5 s prior the end of the process. Then the wet film was annealed at 110 °C for 20 min. MAPbI$_3$; A solution of 620 mg MAPbI$_3$ in 600 μL DMF/DMSO (4/1) was spun at 4000 rpm for 20 s and diethyl ether was dropped at the first 8 s after spin-coating began, followed by annealing at 100 °C for 10 min. For NiO$_x$ as hole transport layer, presynthesized powders of oleophilic NiO$_x$ NPs were dissolved into chloroform/chlorobenzene (2/1) and spin-coated onto perovskite film. For QD intercalation, 5 mg mL$^{-1}$ QDs in octane was spin-coated onto perovskite films, followed by NiO$_x$ deposition. For spiro-OMeTAD as HTL, spiro-OMeTAD dissolved in chlorobenzene (80 mg mL$^{-1}$) with 9.1 mg Li-TFSI and 29 μL tBP, followed by spin-coating at 3500 rpm. Then 60-nm Au electrode was evaporated using thermal evaporation system (Angstrom, SQC-310C) at the speed of 2.5 Å s$^{-1}$ under 3.7 × 10$^{-7}$ vacuum degree with mask of 0.12 cm$^2$ active area.

36-cm$^2$ perovskite solar module—6 × 6 cm$^2$ FTO substrate was scribed into eight separated cells by laser (P1 line). The coating process for each layer was the same as small-area solar cells except for the laser scribing patterning procedure. 280 μm P2 line was scribed after perovskite and NiO$_x$ deposition, using laser with pulse energy of 30 μJ, spot size of 200 μm, and pulse frequency of 30 kHz. 400 μm P3 line was scribed after Au evaporation, using 30 μJ pulse energy. The active area of a 6 × 6 cm$^2$ module was 18 cm$^2$. For the module encapsulation, fabricated module was sealed with a cover glass and polyisobutylene under vacuum, with pressure of 300–400 mTorr for 10 min at 90 °C.

0.12-cm$^2$ semitransparent perovskite solar cell—The deposition of each layer was the same with opaque PSCs on 2 × 2 cm$^2$ FTO. The transparent electrode with construction of MoO$_3$/ITO/Au grid was fabricated layer by layer on perovskite/NiO$_x$ film. 15 nm MoO$_3$ was thermal evaporated with the speed of 1 Å s$^{-1}$ under 5 × 10$^{-7}$ vacuum degree to protect the film from sputtering energy. 150 nm ITO was RF-sputtered with RF magnetron sputtering (Shenyang Kejing, VTC-600-2HD) from a ceramic 2-inch ITO target (90% wt In$_2$O$_3$ and 10% wt SnO, Hefei Kejing) at a pressure of 2 mTorr. The RF-power was maintained at 70 W and the substrate temperature was 70 °C during the 60 min deposition process. 80 nm gold grid was thermally evaporated through a shadow mask to collect the charge carriers and improve conductivity of ITO electrode.

Characterization Methods: Current–voltage characteristics ($J$–$V$ plots) were recorded on a solar simulator equipped with a Keithley 2400 source meter and a 300-W collimated xenon lamp (Newport) calibrated with a light intensity to 100 mW cm$^{-2}$ at AM 1.5 G solar light conditions by a standardsilicon solar cell. The incident photon-to-electron conversion efficiencies (IPCEs) were measured on an external quantum efficiency (EQE) system (Newport) by focusing a monochromatic beam of light onto the devices. The X-ray diffraction (XRD) patterns were analyzed on an X-ray diffraction meter (Rigaku, Ultima IV) with a Cu K$_\alpha$ radiation source. Small angle X-ray scattering (SAXS) spectra were carried out with an Anton-Paar SAXSess mc2. X-ray photoelectron spectroscopy (XPS) spectra were recorded by Thermo Scientific ESCALAB Xi+. An Al K$_\alpha$ (1486.6 eV) X-ray was used as the excitation source. All data were calibrated by C 1s at 284.6 eV. Ultraviolet photoelectron spectroscopy (UPS) was obtained at the same equipment using He (21.2 eV) source with a bias voltage of 5 eV. Scanning electron microscope (SEM) images were recorded using Zeiss Gemini SEM 500 under 5 kV. Energy-dispersive X-ray spectroscopies (EDX) were carried out on the same instrument with Ultrima Extreme detector under 7 kV. Transmission electron microscopy (TEM)
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

interfacial engineering, NiOₓ hole transport layers, n-i-p perovskite solar cells, perovskite quantum dots

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