

Pinhole-Free and Surface-Nanostructured NiO_x Film by Room-Temperature Solution Process for High-Performance Flexible Perovskite Solar Cells with Good Stability and Reproducibility

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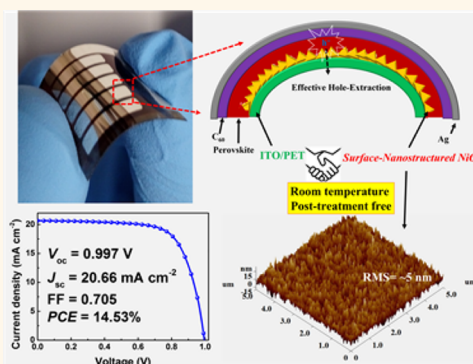
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S Supporting Information

ABSTRACT: Recently, researchers have focused on the design of highly efficient flexible perovskite solar cells (PVSCs), which enables the implementation of portable and roll-to-roll fabrication in large scale. While NiO_x is a promising material for hole transport layer (HTL) candidate for fabricating efficient PVSCs on a rigid substrate, the reported NiO_x HTLs are formed using different multistep treatments (such as 300–500 °C annealing, O_2 -plasma, UVO, etc.), which hinders the development of flexible PVSCs based on NiO_x . Meanwhile, the features of nanostructured morphology and flawless film quality are very important for the film to function as highly effective HTL of PVSCs. However, it is difficult to have the two features coexist natively, particularly in a solution process that flawless film will usually come with smooth morphology. Here, we demonstrate the flawless and surface-nanostructured NiO_x film from a simple and controllable room-temperature solution process for achieving high performance flexible PVSCs with good stability and reproducibility. The power conversion efficiency (PCE) can reach a promising value of 14.53% with no obvious hysteresis (and a high PCE of 17.60% for PVSC on ITO glass). Furthermore, the NiO_x -based PVSCs show markedly improved air stability. Regarding the performance improvement, the flawless and surface-nanostructured NiO_x film can make the interfacial recombination and monomolecular Shockley–Read–Hall recombination of PVSC reduce. In addition, the formation of an intimate junction of large interfacial area at NiO_x film/the perovskite layer improve the hole extraction and thus PVSC performances. This work contributes to the evolution of flexible PVSCs with simple fabrication process and high device performances.

KEYWORDS: perovskite solar cells, hole transport layer, NiO_x nanostructure, room temperature, flexible solar cells



Perovskite solar cells (PVSCs) have drawn enormous attention in the past few years due to the rapid increase of their power conversion efficiencies (PCEs) and prospects for low-cost fabrication.^{1–6} The theoretical limit of the PVSC efficiency has been estimated to be 31% based on the photon recycling effect through detailed balance model,⁷ and a certificated efficiency of 20.1% has recently been achieved.⁸ This shows that PVSCs have great potential to achieve commercialization and replace conventional silicon solar cells in the near future. Currently, many efficient PVSCs use the expensive 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-MeOTAD) as a hole-transporting layer (HTL).^{9–17} However, the spiro-MeOTAD based PVSCs usually employ metal oxide (e.g., TiO_2 ,^{10–15} ZnO ,¹⁶ SnO_2 ¹⁷) as

an electron-transporting layer (ETL), which normally needs a high-temperature (>450 °C) sintering process to achieve efficient carrier-transporting capability. However, the high annealing temperature may be a concern for fabrication on flexible substrates.¹⁸ An alternative to this structure is to place the HTL on the transparent conductive electrode, which is usually called the “inverted” structure. In this structure, fullerene derivatives (e.g., PC_{60}BM ,^{19,20} C_{60} ,^{21,22} IC_{60}BA ²¹) acted as ETL are fabricated without the need for any annealing.

Received: November 7, 2015

Accepted: December 20, 2015

Published: December 20, 2015



NiO_x has been demonstrated to be a promising HTL candidate for fabricating efficient inverted PVSCs on a rigid substrate.^{23–32} The valence band (VB) of NiO_x is well aligned with that of organometallic halide perovskites (e.g., $\text{CH}_3\text{NH}_3\text{PbX}_3$; $\text{X} = \text{I}, \text{Br}, \text{Cl}$) for hole collection/transport. In addition, the wide-bandgap, good optical transparency, and electron-blocking capability make NiO_x a good anode interlayer of PVSC.^{23–32} Furthermore, compared with other organic HTLs,³³ NiO_x is low cost and easy to synthesize. Encouragingly, the PCEs of inverted PVSCs have reached as high as 11.6% with pristine NiO_x and 15.8% with Cu-doped NiO_x .^{30,31} More recently, nanostructured NiO_x has been prepared through pulsed laser deposition (PLD) techniques and employed as an efficient HTL in inverted PVSCs.³² However, all of the reported NiO_x HTLs require sophisticated conditions of high-temperature thermal annealing or a high vacuum procedure during the process of device fabrication. Such stringent conditions will increase the fabrication cost. Meanwhile, a high annealing temperature will make it difficult to fabricate flexible solar cells. Furthermore, the features of nanostructured morphology and flawless film quality are very important for the film to function as highly effective HTL of PVSCs.^{25,32} To the best of our knowledge, there is no report on room-temperature solution-processed NiO_x film with the two features for HTLs of PVSCs or flexible PVSCs,^{18,34} which is challenging and desirable to enable large-scale manufacturing of perovskite optoelectronic devices.

In this work, we demonstrate surface-nanostructured and flawless NiO_x film as HTL for high-performance flexible PVSCs. The surface-nanostructured NiO_x film can be readily formed on various substrates (ITO glass and PET will be demonstrated here) by simple and control room-temperature solution process of NiO_x nanocrystals without any post-treatment. Importantly, our results show that the flawless and surface-nanostructured NiO_x film reduces the interfacial recombination and monomolecular Shockley–Read–Hall recombination of PVSCs. Meanwhile, it provides a large interfacial area with perovskite absorber, which is much more effective in extracting photogenerated holes from the perovskite than a conventional smooth PEDOT:PSS film. Using our surface-nanostructured NiO_x as HTLs, efficient flexible PVSCs with good mechanical stability and reproducibility can also be achieved. The PCE can reach a promising value of 14.53%. Furthermore, a high PCE of 17.60% has been achieved in NiO_x -based PVSC on rigid ITO glass with no obvious hysteresis. Interestingly, the surface-nanostructured NiO_x based PVSCs show better photovoltaic performance and markedly improved air stability compared to those of the PEDOT:PSS-based devices.

RESULTS AND DISCUSSION

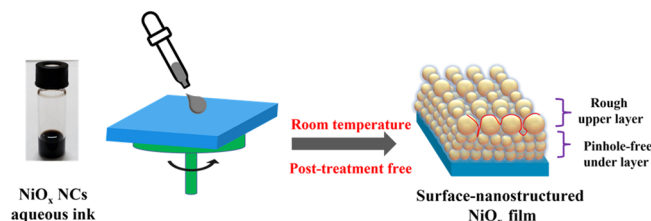
Flawless and Surface-Nanostructured NiO_x Films.

While the features of surface-nanostructured morphology and flawless film quality are different to coexist natively, particularly in a solution-based process, so that a flawless film will usually have smooth morphology,^{35,36} two such features are very important for the film to function as a highly effective HTL of perovskite solar cells.^{25,32} Here, we demonstrate an NiO_x film with these two features simultaneously from our simple room-temperature solution process of nontoxic NiO_x nanocrystals without any post-treatment (e.g., thermal annealing or O_2 plasma or UVO treatments). Interestingly, the NiO_x film with the special features can be formed in both rigid ITO glass and

flexible ITO/PET for favoring a variety of applications of PVSCs. The NiO_x nanocrystals (NCs) were synthesized by a chemical precipitation method.³⁷ The crystalline NiO_x NCs are approximately 4 nm in diameter, as determined by transmission electron microscopy (TEM; Figure S1, Supporting Information). The obtained NiO_x NCs were dispersed into deionized water to synthesize NiO_x NC aqueous ink with different concentrations.

Scheme 1 shows the process of our new approach for fabricating nanostructured NiO_x film. The stacked NiO_x

Scheme 1. Schematic Illustration of Our New Approach for Fabricating Surface-Nanostructured NiO_x Films



nanostructures were readily formed by spin-coating the NiO_x NCs aqueous inks onto the precleaned ITO substrate and dried naturally at room temperature. The resultant NiO_x films could be used to fabricate solar cells without annealing or other O_2 -plasma or UVO treatments.

The quality of the NiO_x films can be controlled by tuning the concentration of NiO_x NC inks. The thicknesses of the corresponding NiO_x films were measured to be ca. 8 nm (1.0 wt %), 12 nm (1.5 wt %), 19 nm (2.0 wt %), 22 nm (2.5 wt %), and 27 nm (3.0 wt %) by ellipsometry. The morphology of the NiO_x films was examined by using atomic force microscopy (AFM) and scanning electron microscope (SEM). Note that the surface of pristine ITO is very smooth with a root-mean-square (RMS) roughness of 1.00 nm (see Figure 1a). Interestingly, as shown in Figure 1b–f, the resulting NiO_x films create surface roughness in nanometer scale. The surface roughness increases by ca. 4.3 nm when the ITO is covered by the NiO_x films. Surprisingly, the surface roughness of the NiO_x films does not show any clear change with the variation of thickness, which indicates that the nanostructures of NiO_x films can be robustly formed for use in PVSCs.

We further study the characters of NiO_x films by SEM, as shown in Figure 2. When the concentration of NiO_x NCs was low (1.0 and 1.5 wt %), some pinholes appeared in the NiO_x films (Figures 2a–c), and thus, there was a high probability of forming direct contact between perovskite and ITO, which may make for less effective electron blocking and more serious carrier recombination. After slightly increasing the concentration of NiO_x NCs, a flawless NiO_x film can be obtained (Figure 2d,e and Figure S2). As shown in Figure 2f, the flawless NiO_x films also have a nanostructured surface. These surface-nanostructured NiO_x films could form an intimate junction of large interfacial area with the perovskite layer, which can be beneficial to extract photogenerated electrons from the perovskite absorber.^{25,32}

We also studied the effect of film quality of NiO_x on the device performance. As shown in Figure 3a, the flawless NiO_x film cast from 2 wt % of NiO_x NC ink with an appropriate thickness of 20 nm achieves the best device performance. When NiO_x NC ink concentration increases from 1.0 wt % to 2.0 wt %, the device open-circuit voltage (V_{oc}) increases from 0.88 to

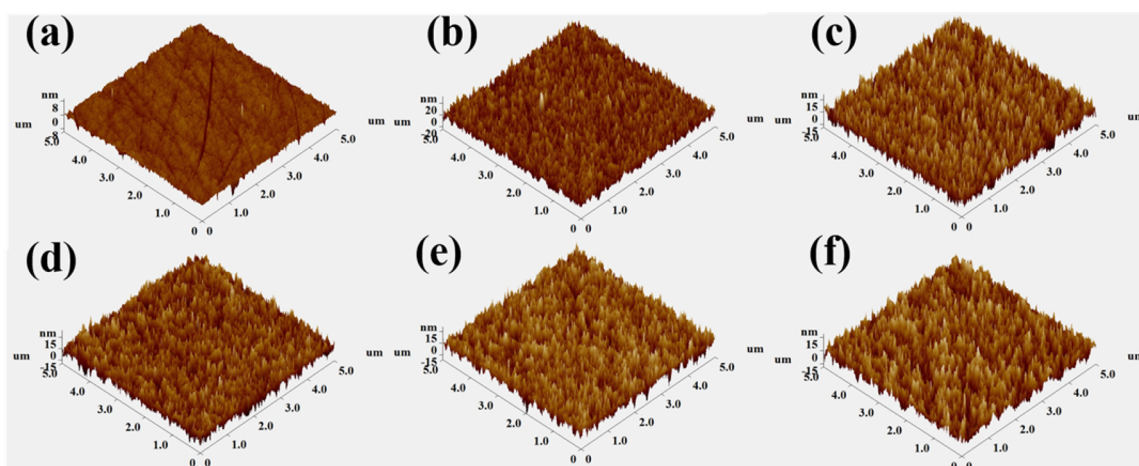


Figure 1. AFM three-dimensional view of (a) pristine ITO substrate and NiO_x films cast on ITO substrates from (b) 1.0 wt %, (c) 1.5 wt %, (d) 2.0 wt %, (e) 2.5 wt %, and (f) 3.0 wt % NiO_x NC inks. The RMS roughness values are 1.0, 5.38, 5.44, 5.32, 5.23, and 5.18 nm, respectively. RMS = root mean square.

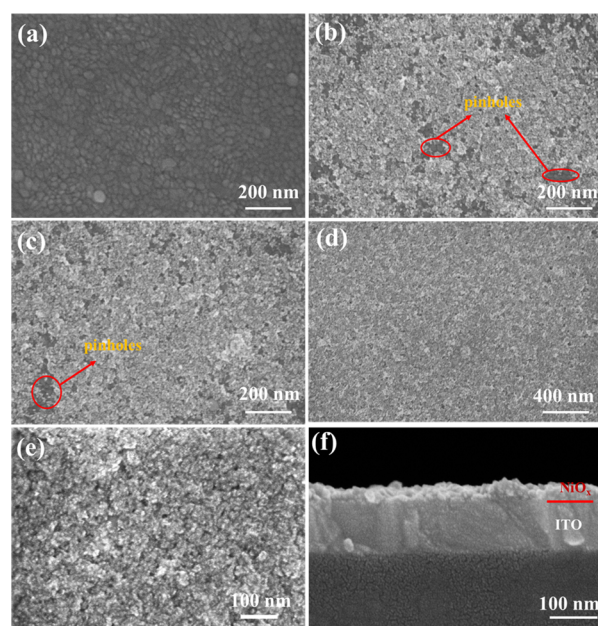


Figure 2. Top-view SEM image of ITO (a); NiO_x films cast on ITO substrates from (b) 1.0 wt %, (c) 1.5 wt %, (d, e) 2.0 wt % NiO_x NC inks. (f) Cross-sectional SEM image of NiO_x film prepared from 2.0 wt % NiO_x NC ink.

0.94 V with thicker NiO_x films. The improved V_{oc} value may be attributed to the elimination of pinholes and formation of flawless NiO_x film which can better block electrons and reduce leakage current. In contrast, with NiO_x NC ink concentration increasing from 2.0 wt % to 3.0 wt %, although the NiO_x films are flawless, the short-circuit current density (J_{sc}) decreases from 19.24 to 18.32 mA cm^{-2} , which leads to a lower PCE. The increased series resistance induced by a thicker NiO_x film is most likely the main reasons for the current reduction.

Figure 3b reveals the optical transmission spectra of the optimal surface-nanostructured NiO_x films on different conductive substrates in this study. Both NiO_x films on the ITO/glass and ITO/PET show high transmittance >76% on average in the wavelength range 400–800 nm, allowing maximum photo flux to reach the absorber layer for photogenerated carriers.

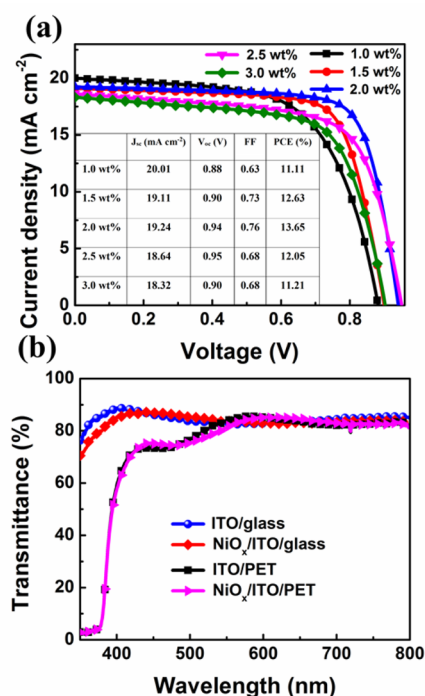


Figure 3. (a) J - V curves of PVSCs fabricated from different concentrations of NiO_x NC inks. (b) The optical transmission spectra of the ITO/glass, ITO/PET, NiO_x /ITO/glass, and NiO_x /ITO/PET films. The NiO_x films with the thickness of 20 nm were prepared from 2.0 wt % NiO_x NC inks.

The chemical component of the NiO_x films was investigated by X-ray photoelectron spectroscopy (see Figure S3). The background was subtracted from the XPS spectra by using a Shirley-type background subtraction. The decomposition of the XPS spectrum demonstrated that the Ni 2p spectrum can be well fitted by two different oxidation states (Ni^{2+} and Ni^{3+}) in the form of a Gaussian function, and rather remarkable contributor peaks of Ni^{3+} state such as NiOOH (Ni 2p_{3/2} at 856.0 eV and O 1s at 532.3 eV), Ni_2O_3 (Ni 2p_{3/2} at 855.0 eV, and O 1s 530.9 eV), and another Ni^{2+} state NiO (Ni 2p_{3/2} at 853.7 and O 1s 529.2 eV) appeared. As calculated from the integral area in the Ni 2p spectrum, the three composition

concentration ratio of NiOOH , Ni_2O_3 , and NiO is about 0.75:0.81:1, which illustrates that the composition of the nickel oxide is nonstoichiometric.

Efficient Flexible PVSCs with Excellent Reproducibility. No treatment is needed for formation of our surface-nanostructured NiO_x films, which inspired us to fabricate flexible PVSCs using the NiO_x HTLs on flexible ITO/PET substrate. The device structure for this study is illustrated in Figure 4a. The relevant energy levels of each layer in the device

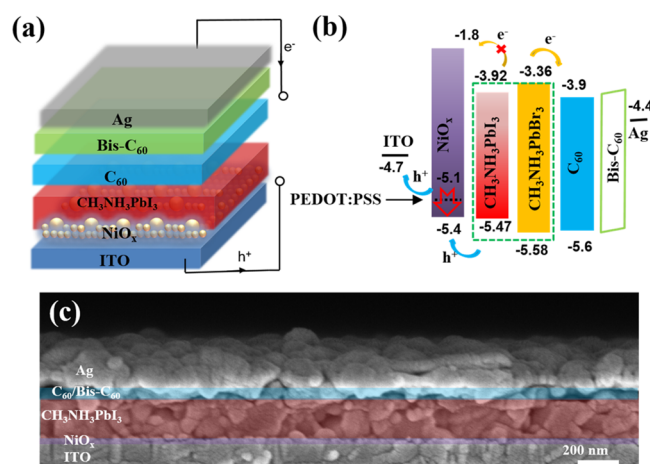


Figure 4. (a) Device structure of PVSCs in this study and (b) corresponding energy band diagram relative to the vacuum level. (c) Cross-sectional SEM image of an optimized NiO_x -based device.

are depicted in Figure 4b. Compared to conventional HTL PEDOT:PSS (VB of ~ -5.1 eV), NiO_x has a deeper VB of ~ -5.4 eV (determined by ultraviolet photoelectron spectroscopy (UPS)), which is much closer to that (-5.47 eV) of $\text{CH}_3\text{NH}_3\text{PbI}_3$ and (5.58 eV) of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ ^{2,9} and, thus, will create a suitable ohmic contact. In particular, given that the CB of NiO_x (-1.8 eV) is significantly closer to the vacuum level compared with that of perovskite,² NiO_x is also able to efficiently prevent electron leakage. In addition, the lowest unoccupied molecular orbital (LUMO) of C_{60} (-3.9 eV) matches well with the CB of the perovskite, which allows efficient electron transport to the external circuit. The bis- C_{60} surfactant is employed as an efficient electron-selective interfacial layer that aligns the energy levels at the organic/cathode interface.³⁸ Figure 4c shows a typical SEM image of the complete device using NiO_x as HTLs.

Figure 5a shows the current density–voltage (J – V) curves of the PVSCs using both flexible ITO/PET and rigid ITO/glass substrates under AM 1.5G irradiation. The key J – V parameters of the devices are summarized in Table 1. The NiO_x -based flexible PVSC exhibits a V_{oc} of 0.997 V, a J_{sc} of 20.66 mA cm^{-2} , and a fill factor (FF) of 0.705, corresponding to a high PCE of 14.53%. In addition, to obtain a reliable PCE as suggested by Snaith and coworkers,³⁹ we can measure the steady-state current density of our NiO_x based device at the maximum power point (0.79 V) under irradiation. As shown in Figure S4, the photocurrent stabilizes within seconds to approximately 18.35 mA cm^{-2} , yielding a stabilized PCE of 14.50%. To the best of our knowledge, this is the first time for such high PCE to be demonstrated in flexible PVSCs with NiO_x HTL. The rigid NiO_x based PVSC shows a V_{oc} of 1.03 V, a J_{sc} of 21.80 mA cm^{-2} , a FF of 0.784, yielding a high PCE of 17.60% with a stabilized PCE of 17.50% (see Figure S5). A careful study

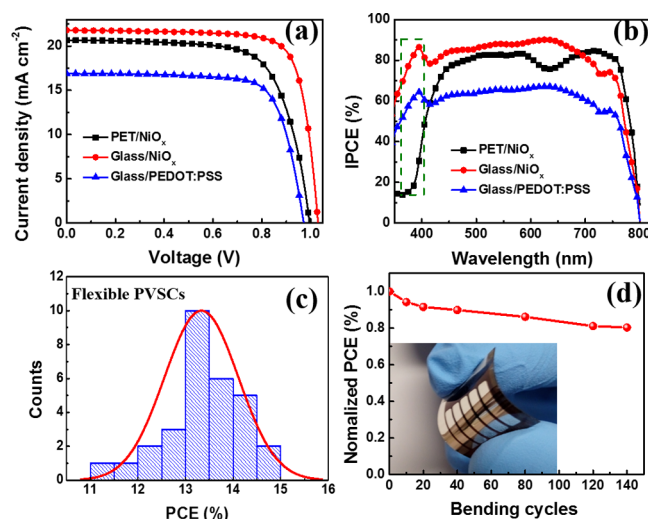


Figure 5. (a) J – V curves; (b) IPCEs for the best PVSCs using different HTLs on flexible and rigid substrate. (c) The PCE distribution histogram of NiO_x -based flexible PVSCs. (d) Normalized PCE of NiO_x -based flexible PVSCs as a function of bending cycles and the photograph of a NiO_x -based flexible PVSC (inset).

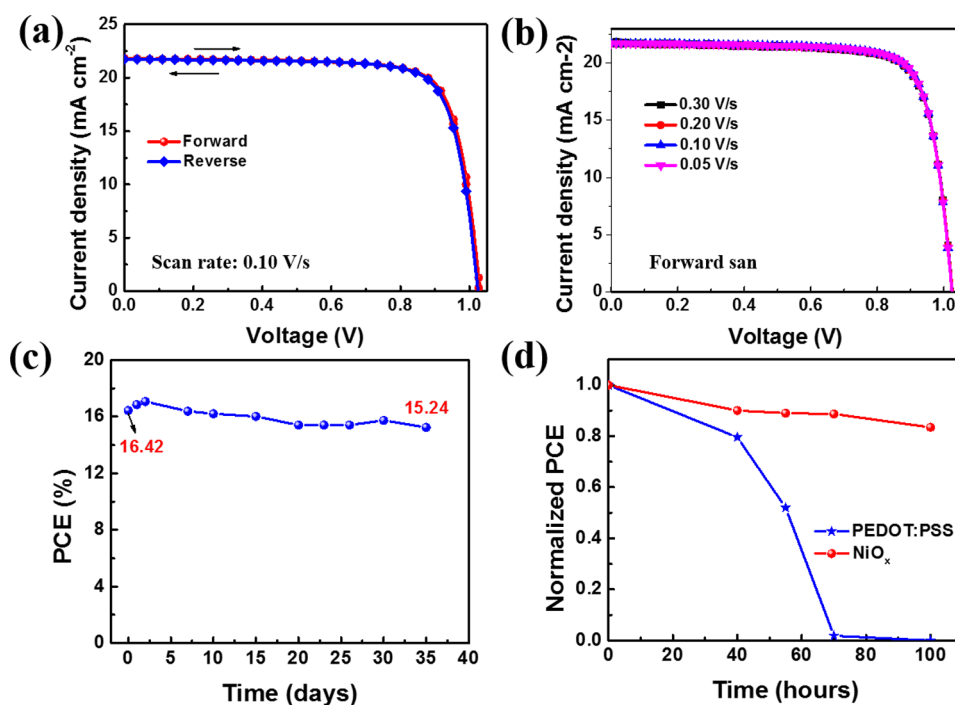
shows that the slightly lower PCE comparing to that of the rigid device is due to the decreased J_{sc} and FF, likely caused by the higher series resistance and lower transmittance of the PET/ITO substrate in short wavelength spectrum (Figure 3b). Figure 5b confirms that the photon-to-electron conversion efficiency (IPCE) of the flexible device displays a lower response at the long wavelength region leading to a substantial loss of photocurrent between 300 and 500 nm. Using highly transparent Ag nanowire flexible conductive substrate to replace the conventional PET/ITO flexible substrate may overcome this drawback in the near future.⁴⁰ Notably, our NiO_x based flexible PVSCs show a good reproducibility with limited variation as shown in Figure 5c. The histogram of solar cell efficiencies is collected from 30 samples of NiO_x -based flexible PVSCs. Approximate 70% of the cells show PCE over 13% with the average PCE reaches 13.33% (see Table 1). In addition, we have performed mechanical bending tests. As shown in Figure 5d, the performance of the device retains over 80% of its initial efficiency even after 100 bending cycles, indicating that the NiO_x based flexible PVSCs show good mechanical stability.

Device Hysteresis and Stability. Recently, significant hysteresis of J – V curves in the PVSCs has been widely reported and considered as a critical issue for photovoltaic performance. Although the origins for the hysteresis of PVSCs have not been fully understood, several possible mechanisms, including phase transition, ferroelectric property, defects in the perovskite, and charge accumulation within the device, have been demonstrated by several research groups.^{40–42} To better understand the hysteresis of our NiO_x -based PVSCs, we measured the devices under different scan directions and scan rates. The corresponding J – V curves are shown in Figure 6a,b, and the photovoltaic parameters are summarized in Table S1. Notably, our NiO_x -based devices exhibited negligible hysteresis. The negligible hysteresis of the NiO_x -based device should be due to the fullerene effect, which is in good agreement with the previous study.⁴²

Besides the efficiency, stability is another important issue in PVSCs, which restricts their outdoor photovoltaic applications.

Table 1. Photovoltaic Performance Parameters Extracted from J – V Measurements under Standard AM 1.5 Illumination (100 mW cm^{-2})^a

substrate/HTLs ^a	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
PET/ITO/ NiO_x	0.97 ± 0.01	20.55 ± 0.71	0.68 ± 0.03	13.33 ± 0.78
Best	1.00	20.66	0.705	14.53
glass/ITO/ NiO_x	1.01 ± 0.03	20.57 ± 0.95	0.76 ± 0.03	15.87 ± 0.89
Best	1.03	21.80	0.784	17.60
glass/ITO/PEDOT:PSS	0.95 ± 0.02	15.01 ± 0.95	0.72 ± 0.03	10.37 ± 0.74
Best	0.98	16.89	0.740	12.28

^aThe statistics is determined from 30 devices.**Figure 6.** J – V curves for the best NiO_x -based PVSCs measured under different scan directions (a) and different scan rates (b). The PCE evolution of an encapsulated NiO_x -based device stored for different numbers of days (c). The air stability of the unencapsulated devices with NiO_x or PEDOT:PSS (d).

Therefore, we also checked the air stability of our NiO_x -based devices. The encapsulated device was kept in ambient air and dark conditions to test the stability. As shown in Figure 6c, the resulting NiO_x -based device demonstrated good stability over a period of 30 d and maintained 93% of its initial efficiency. Additionally, compared with conventional PEDOT:PSS-based devices, the unencapsulated NiO_x based PVSCs also exhibited better air stability (see Figure 6d). The fast degradation of PEDOT:PSS-based device should be due to the acidic and hygroscopic characteristics of PEDOT:PSS that damage the ITO electrode and the adjacent moisture-sensitive absorber ($\text{CH}_3\text{NH}_3\text{PbI}_3$).

Contributions of the Flawless and Surface-Nanostructured NiO_x HTL. To better understand the outstanding performance of our NiO_x control devices using PEDOT:PSS as HTL were also fabricated on ITO/glass substrate. The J – V curve of the best PEDOT:PSS based reference device is depicted in Figure 5a. Their corresponding photovoltaic parameters are also summarized in Table 1. Interestingly, all the NiO_x -based devices show an average efficiency of 15.87% with the best PCE of 17.60% under 1 sun condition. On the other hand, the PEDOT:PSS-based cells show an average efficiency of 10.37% with only 12.28% as the most efficient

device. Histograms of the device performance are presented in the Supporting Information (Figure S6). It was found that the IPCE of NiO_x -based PVSCs is also higher than that of PEDOT:PSS-based PVSCs, particularly from 400 to 750 nm (Figure 5b). The major improvement lies in the increased J_{sc} , which can be attributed to more efficient hole extraction and electron blocking of NiO_x than PEDOT:PSS.

To gain more insight into the contributions of our NiO_x films, we have investigated the charge-extraction property and the dominant recombination mechanisms that influences photovoltaic performance of PVSCs. First, we have conducted steady-state photoluminescence (PL) measurements to study the efficiency of charge extraction of different HTLs. As illustrated in Figure 7a, the NiO_x film exhibits more efficient PL quenching than PEDOT:PSS, indicating its better hole extraction capability from perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$. The time-resolved photoluminescence (TRPL) profiles in Figure 7b show that the PL decay rate of $\text{CH}_3\text{NH}_3\text{PbI}_3$ is also higher for NiO_x . The PL decay curves were fitted using a biexponential equation (eq 1).

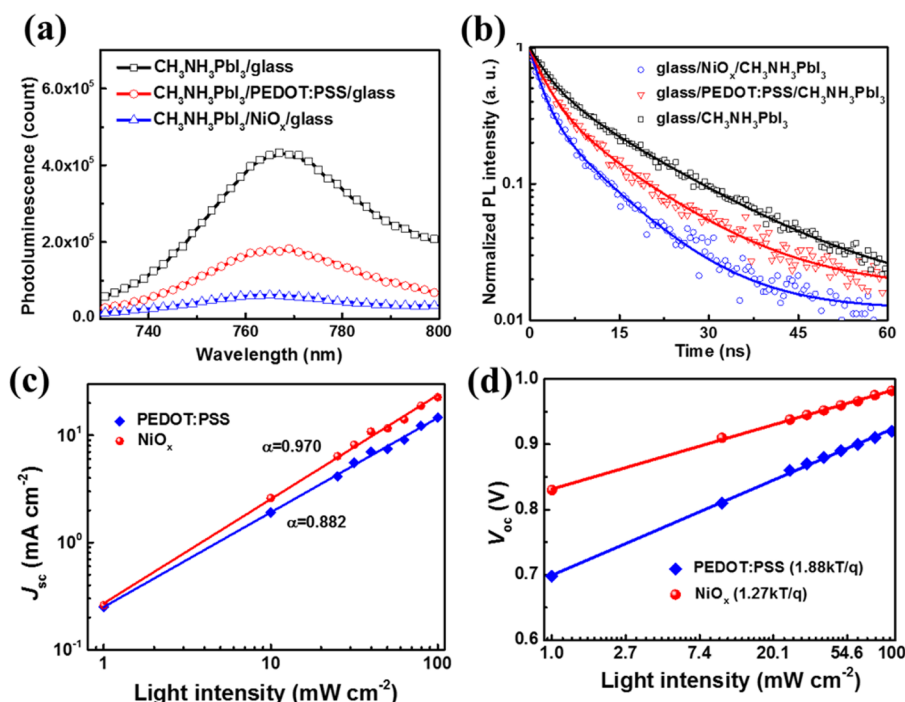


Figure 7. (a) Steady-state and (b) time-resolved photoluminescence spectra of CH₃NH₃PbI₃ films on bare glass, NiO_x, and PEDOT:PSS. Light intensity-dependence of CH₃NH₃PbI₃-based PVSCs with NiO_x and PEDOT:PSS as HTL for (c) J_{sc} dependence upon different light intensities and (d) V_{oc} dependence upon different light intensities.

$$I(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (1)$$

The average recombination lifetimes (τ_{avg}) are estimated with the τ_i and A_i values from the fitted curve data (Table S2) using eq 2.

$$\tau_{avg} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i} \quad (2)$$

The average PL lifetime (τ_{avg}) of CH₃NH₃PbI₃ on glass was estimated to be 10.0 ns, while it decreased to 7.0 and 4.8 ns when it was deposited on top of PEDOT:PSS and NiO_x, respectively. This result validates that faster and more efficient hole-extraction is achieved at the NiO_x/CH₃NH₃PbI₃ interface, which contributes significantly to the high J_{sc} value for the PVSCs using nanostructured NiO_x as HTL.

In addition to the J_{sc} , the increased V_{oc} of the NiO_x-based devices should be attributed to minimized potential loss at the interface of HTL/perovskite because of their better energy alignment (we also verified this finding in the CH₃NH₃PbBr₃ system, which has a deeper VB of -5.58 eV as shown in Figure S7.) and lower recombination kinetics. To verify this hypothesis, we have further studied the light intensity dependence of the J - V characteristics of the PVSCs to probe the dominant recombination mechanisms. Figure 7c presents the power law dependence of the J_{sc} with light intensities ($J = I^\alpha$). According to previous studies, a solar cell that is space charge limited due to a carrier imbalance or an interfacial barrier will have a power law relationship with $\alpha = 0.75$. However, a device with an ignorable space charge limit has α value toward to 1. The α for NiO_x-based PVSCs was fitted to be 0.970, indicating it is not space charge limited. On the other hand, the PEDOT:PSS-based PVSCs have an α value of 0.882. This higher slope value for the NiO_x-based device indicates that

the surface-nanostructured NiO_x HTL significantly mitigates the interfacial recombination loss at the HTL/CH₃NH₃PbI₃ interface.

Since all of the photogenerated charge carriers in the perovskite layer will eventually recombine within the cell under open-circuit conditions, studying the relation between the V_{oc} and the light intensity is a powerful tool to probe the recombination mechanisms precisely. Generally, if bimolecular recombination (the recombination of free electrons and holes in the photoactive layer) is dominant, the slope of V_{oc} versus light intensity will be close to kT/q , where q is the electron charge, k is the Boltzmann constant, and T is the kelvin temperature. While the slope is greater than kT/q , V_{oc} will become strongly depend on light intensity, additional interfacial trap-assisted Shockley-Read-Hall (SRH) recombination is involved.⁴³ As shown in Figure 7d, NiO_x-based PVSCs have a slope value of 1.27kT/q, indicating a weaker V_{oc} dependence on the light intensity than the PEDOT:PSS-based device (1.88kT/q). As a consequence, we can conclude that NiO_x film effectively reduces the monomolecular SRH recombination, which is critical to improve device performance.

It is worthwhile to note that the morphology and crystallinity of CH₃NH₃PbI₃ layers on both surface-nanostructured NiO_x and PEDOT:PSS are quite similar (see Figure S8 in the Supporting Information), which further indicates the improved performance of the nanostructured NiO_x-based PVSCs are mainly attributed to the efficient charge extraction and reduction of the monomolecular SRH recombination at the NiO_x/CH₃NH₃PbI₃ interface. As a consequence, all these results discussed above demonstrate the potential of our flawless and surface-nanostructured NiO_x as an efficient HTL for achieving high-performance and stable perovskite solar cells.

CONCLUSION

In summary, we have demonstrated a controllable approach to form surface-nanostructured and flawless NiO_x film as HTL for high-performance flexible PVSCs through a room-temperature, solution-processing technique. The flawless and surface-nanostructured NiO_x film reduces the interfacial recombination and monomolecular Shockley–Read–Hall recombination of PVSCs and provides an intimate junction of large interfacial area with the perovskite layer, which is much more effective in extracting photogenerated holes from the perovskite than a conventional smooth PEDOT:PSS film. As a result, NiO_x -based flexible PVSCs with good stability and reproducibility have been realized on ITO/PET flexible substrate. The PCE can reach a promising value of 14.53%. Encouragingly, a remarkable efficiency of 17.60% could be achieved on glass/ITO rigid substrate with a high FF of 0.784, a J_{sc} of 21.80 mA cm^{-2} , and a V_{oc} of 1.03 V with no obvious hysteresis. Importantly, compared with the conventional PEDOT:PSS based PVSCs, the NiO_x based devices showed higher photovoltaic performance and better air stability. This study opens a new way for the design of high performance PVSCs and also paves the way toward industrial scalable roll-to-roll manufacturing of PVSCs.

METHODS

NiO_x NC Ink Synthesis. NiO_x NCs were synthesized according to our previous report.³⁷ Briefly, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mol) was dispersed in 100 mL of deionized water to obtain a dark green solution. The pH of the solution was adjusted to 10 by adding a NaOH solution (10 mol L^{-1}). After being stirred for 5 min, the colloidal precipitation was thoroughly washed with deionized water twice, and dried at 80°C for 6 h. The obtained green powder was then calcined at 270°C for 2 h to obtain a dark-black powder. The NiO_x NCs inks were prepared by dispersing the obtained NiO_x NCs in deionized water to different concentrations.

Materials. All of the chemicals and materials were purchased and used as received unless otherwise noted. PEDOT:PSS (Baytron AL 4083) was purchased from H. C. Starck GmbH, Germany. $\text{CH}_3\text{NH}_3\text{I}$ was purchased from Dyesol and used as received. PbI_2 (99%) was purchased from Sigma-Aldrich. Bis- C_{60} surfactant was provided by Prof. Alex K.-Y. Jen.³⁸

Device Fabrication. ITO-coated glass substrates or ITO-coated PET substrates were cleaned and then ultraviolet-ozone treated for 20 min. PEDOT:PSS (Baytron AL 4083) was spin-coated with thickness of 45 nm and then dried at 150°C for 10 min. The NiO_x NCs ink (20 mg/mL in DI-water) was spin-coated to obtain $\sim 20 \text{ nm}$ NiO_x film. The resultant NiO_x films were used to fabricate devices without an annealing process or other treatments. The $\text{CH}_3\text{NH}_3\text{PbI}_3$ solutions were prepared by reacting the $\text{CH}_3\text{NH}_3\text{I}$ powder and PbI_2 in γ -butyrolactone/DMSO = 7:3 (v/v) at 60°C for 1 h. Similarly, the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ solutions were prepared by reacting the $\text{CH}_3\text{NH}_3\text{Br}$ powder and PbBr_2 in γ -butyrolactone/DMSO = 7:3 (v/v) at 60°C for 1 h. The 1 M perovskite precursor solution was deposited onto a NiO_x /ITO or PEDOT:PSS/ITO substrate by a consecutive two-step spin-coating process at 1000 rpm and at 4000 rpm for 20 and 40 s, respectively, and $180 \mu\text{L}$ of toluene was rapidly poured on top of the substrates during spin coating in the second spin stage which is slightly modified method from the reported protocol.⁴³ The perovskite precursor coated substrate was dried on a hot plate at 100°C for 10 min. Subsequently, the C_{60} (20 mg/mL in dichlorobenzene) and bis- C_{60} surfactant (2 mg/mL in isopropyl alcohol) were then sequentially deposited by spin coating at 1000 rpm for 60 s and 3,000 rpm for 30 s, respectively. Finally, the device was completed with the evaporation of Ag contact electrodes (120 nm) in a high vacuum through a shadow mask. The active area of this electrode was fixed at 0.06 cm^2 . All devices were fabricated in glovebox.

Measurement and Characterization. Solar-simulated AM 1.5 sunlight was generated using a Newport AM 1.5G irradiation (100

mW/cm^2) calibrated with an ISO 17025-certified KG3-filtered silicon reference cell. The spectral mismatch factor was calculated to be less than 1%. The J – V curves were recorded using a Keithley 2635 apparatus. SEM images were recorded using a LEO 1530 scanning electron microscope. The steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra of the samples were measured according to our previous method.^{15,20} Transmittance measurements were performed under a dark ambient environment using spectroscopic ellipsometry (Woollam).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.5b07043.

TEM image of NiO_x NCs, XPS elemental analysis, and AFM phase image of NiO_x film, stabilized PCE and hysteresis measurement of NiO_x -based devices, histograms of the PCE for PVSCs based on different HTL, TRPL measurement, J – V characteristics of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ solar cells, SEM images, and AFM topography of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film on different HTLs (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the University Grant Council of the University of Hong Kong (Grant No. 104003113), the General Research Fund (Grant No. HKU711813), the Collaborative Research Fund (Grant Nos. C7045-14E, CUHK1/CRF/12G) from the Research Grants Council of Hong Kong Special Administrative Region, China, and Grant No. CAS14601 from the CAS–Croucher Funding Scheme for Joint Laboratories. K.S.W. acknowledges the financial support of AoE/P-02/12 from the Research Grants Council of Hong Kong. A.K.Y.J. acknowledges support from the Office of Naval Research (N00014-14-1-0170) and the Asian Office of Aerospace R&D (FA2386-11-1-4072).

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