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Comparison of NiO_x thin film deposited by spin-coating or thermal evaporation for application as a hole transport layer of perovskite solar cells†

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We compared nickel oxide (NiO_x) deposited by thermal evaporation and that deposited by the spin-coating process, for use in the hole transport layers of inverted planar perovskite solar cells (PSCs). Spin-coating deposition for NiO_x HTL has been widely used, owing to its simplicity, low cost, and high efficiency. However, the spin-coating process has a technical limit to depositing a large-area uniformly. In contrast, thermal evaporation fabrication has a low price and is able to produce uniform and reproducible thin film. Hence, the chemical states, energy band alignment, surface morphologies, and microstructures of NiO_x deposited by spin coating and thermal evaporation were analyzed. The PSC with NiO_x HTL deposited by thermal evaporation showed a higher power conversion efficiency of 16.64% with open circuit voltage 1.07 V, short circuit current density of 20.68 mA cm⁻², and a fill factor of 75.51% compared to that of PSC with spin-coated NiO_x. We confirmed that thermal evaporation can deposit NiO_x to give a better performance as a HTL with higher reproducibility than spin-coating.

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1 Introduction

Renewable energy is considered a solution for climate change that is causing critical problems such as a sea level rise, and famine. Among the power generation technologies using renewable energy, the photovoltaic cell is a promising technology that converts infinite solar energy into electrical energy. Organic-inorganic halide perovskite solar cells (PSCs) have received attention owing to a remarkable increase in power conversion efficiency (PCE) from 3.8% in 2009, to 25.2% recently.¹⁻⁶ Organic-inorganic perovskite is represented by the general formula ABX₃, where A is an organic/inorganic monovalent cation (methylammonium (CH₃NH₃⁺), formamidinium (NH₂CH₃NH₂⁺), Cs⁺ or Rb⁺), B is a divalent metal cation (Pb²⁺ or Sn²⁺), and X is a monovalent halide anion (Cl⁻, Br⁻ or I⁻).⁷⁻⁹ Perovskite material is suitable to apply to the solar cell, due to its optical and electronic properties. Perovskite has higher absorption coefficient of $\alpha > 105 \text{ cm}^{-1}$ and lower exciton binding energy of 30–50 meV than other photovoltaic materials. Because of these properties, the light absorption layer of the

PSC is able to generate a lot of electric charge, even at relatively thin thickness. Moreover, the charge in the perovskite layer is easy to move to the charge transport layer, because of the high diffusion carrier mobility of $10\text{--}60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, long carrier lifetime of $\sim 100 \text{ ns}$ and long-range diffusion lengths ($\sim 1 \text{ }\mu\text{m}$) of the perovskite layer.¹⁰⁻¹³ The PSC has a structure by which the active perovskite layer is located between the electron transport layer (ETL) and the hole transport layer (HTL), and PSCs are divided into mesoscopic and planar devices, according to the form of the charge transport layer. PSCs are also divided into n-i-p or p-i-n structures, depending on the direction of incident light. If the incident light is through the HTL, it is defined by p-i-n structure. Among these, the p-i-n planar device has been widely studied, due to advantages such as low cost, easy fabrication process, low temperature process, long-term stability and negligible hysteresis effects.¹⁴⁻¹⁸

In the interest of improvement in the properties of PSCs, it is important to select the HTL material. From a high-stability point of view, p-type metal oxide with high durability is a suitable candidate for the HTL.^{15,19} One of the most studied p-type metal oxides for HTL is nickel oxide (NiO_x), due to its abundance and chemically stable nature.¹⁶ Moreover, NiO_x compounds have large bandgap and a deep-lying valance band that cause favorable energy level alignment with the perovskite active layer.^{14,16,20} NiO_x can be synthesized by various kinds of methods,¹⁴ such as solution process,^{21,22} magnetron sputtering process,²³ pulsed laser deposition,²⁴ and electron-beam-evaporation.²⁵ Among them, spin-coating, using NiO nanoparticles suspension, has been widely used, owing to its simplicity, and

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low cost. For example, Liu *et al.* fabricated NiO_x layers using spin-coating for the HTL of PSCs, and obtained a PCE of 15.89%.²⁶ However, the spin-coating process has a technical limit to uniform deposition large-area and upscaling for solution-based processes is difficult to optimize, because it is greatly affected by deposition condition, such as wetting behavior and solvent evaporation.²⁷ Although magnetron sputtering, atomic layer deposition, and laser deposition can obtain uniform and reproducible NiO_x thin films, the processing cost is highly increased.²⁸ But the thermal evaporation is a low-cost fabrication process, and it is able to obtain the desired uniformity and reproducibility of thin film.²⁹

In this work, we compared properties, such as structure, energy band level, transmittance, and surface morphology, of NiO_x film deposited by thermal evaporation or spin-coating processes on ITO electrode. NiO_x deposited by thermal evaporation (thermal- NiO_x) and NiO_x deposited by spin-coating (spin- NiO_x) were applied to PSCs as HTL, and their photovoltaic performances were compared to substitute typical spin- NiO_x HTL with thermal- NiO_x .

2 Experimental

2.1 Preparation of NiO_x thin films

Fig. 1(a) shows a schematic fabrication process by which NiO_x is deposited by thermal evaporation and spin-coating processes on the indium tin oxide (ITO) anode. The substrate ($2.5 \times 2.5 \text{ cm}^2$) with pre-coated ITO anode underwent UV/ozone treatment for 30 min before the deposition of thermal- NiO_x , and coating of spin- NiO_x HTL on top of ITO anode. Thermal- NiO_x was deposited 5 nm thick by evaporating NiO granules (>99.9%, 3–12 mm) in the thermal evaporator maintaining a vacuum condition of 1×10^{-6} torr and deposition rate less than

0.2 \AA s^{-1} . We conducted study on the performance of perovskite solar cell according to thickness of thermal- NiO_x , as shown in Fig. S1,† and the optimum thickness was set at 5 nm based on the results. Spin- NiO_x was deposited that was 30 nm thick by spin-coating NiO nanoparticle solution at 4000 rpm for 40 s, then, it was annealed at 300°C for 30 min in air. Fig. 1(b) shows a photograph of each sample after deposition.

2.2 Characterization of the NiO_x HTL

The chemical states of NiO_x thin films were investigated by a X-ray photoelectron spectroscopy (K-alpha, ThermoScientific). The energy band alignments of NiO_x thin films were confirmed by UV/visible spectroscopy (Lambda 750, PerkinElmer) and ultraviolet photoelectron spectroscopy (NEXSA, ThermoScientific) measurement. The surface morphologies of NiO_x thin films and perovskite layers were investigated by field emission scanning electron microscopy (JSM-7600F, JEOL) and atomic force microscope (n-Tracer, NanoFocus) analysis. The microstructures and interface between NiO_x thin film and perovskite were analysed by high resolution transmittance electron microscope (JEM-2100F, JEOL). The device performance of solar cells with NiO_x HTL was measured using a solar simulator (Oriel Sol3A, Newport) with AM 1.5 G irradiation.

2.3 Fabrication and evaluation of PSCs with NiO_x HTL

To evaluate the performance of NiO_x as HTL of PSCs, p-i-n PSCs was fabricated. Immediately before perovskite deposition, thermal- NiO_x was annealed continuously annealed from room temperature to 330°C and annealed for 1 min after reaching 330°C . Because, as shown Fig. S2,† thermal- NiO_x has poor wettability for perovskite solution. Then, the perovskite layer was deposited on NiO_x HTL from a precursor solution prepared by mixing formamidinium iodide (FAI, 1.09 M), cesium iodide (CsI, 0.25 M), methylammonium bromide (MABr, 0.11 M), lead(II) iodide (PbI_2 , 1.23 M), and lead(II) bromide (PbBr_2 , 0.22 M) in *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) (8 : 2 v/v). The perovskite precursor solution was spin-coated by continuous two-step process at 500 rpm for 5 s, and 5000 rpm for 45 s. The perovskite precursor solution was spin-coated by continuous two-step process at 500 rpm for 5 s, and 5000 rpm for 45 s. During the second coating step, 0.4 mL of anhydrous chlorobenzene was dropped onto the spinning substrate after 15 s, then annealed at 100 for 30 min. After that, C_{60} , SnO_2 , and Ag layers were sequentially deposited on a perovskite layer by thermal evaporation process. As electron transport layer, C_{60} was deposited 35 nm with deposition rate of 0.6 \AA s^{-1} and SnO_2 was deposited 3.5 nm with rate 0.1 \AA s^{-1} . Finally, 120 nm Ag was deposited as electrode on top. All thermal evaporation processes were performed in maintaining a vacuum condition of 1×10^{-6} torr.

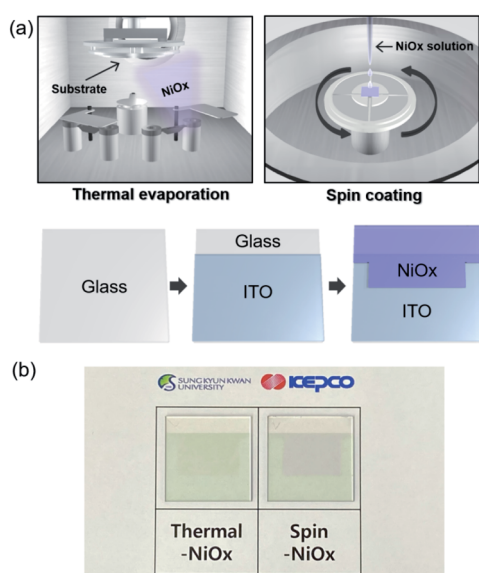


Fig. 1 (a) Schematic of the fabrication process of the patterned NiO_x /ITO anode on glass for the perovskite solar cell. (b) Photograph of NiO_x /ITO samples deposited by thermal evaporation or spin-coating.

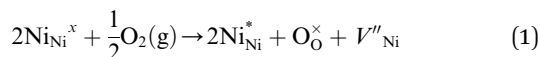
3 Results and discussion

3.1 Chemical states of NiO_x thin films

The X-ray photoelectron spectroscopy (XPS) measurements were performed to compare the chemical states and stoichiometries



of thermal-NiO_x and spin-NiO_x HTL. Because of its wide bandgap, the stoichiometric form of NiO is an insulator with a very low intrinsic conductivity of 10⁻¹³ cm⁻¹ at room temperature.^{30,31} But, NiO is a metal-deficient p-type semiconductor, so Ni vacancies are present at the cation lattice site. Due to Ni vacancies, some Ni²⁺ ions have to be converted to Ni³⁺ ions in order to maintain the electrical neutrality in the structure, and the created Ni³⁺ ions take charge of conduction in NiO.³²⁻³⁶ The creation of Ni³⁺ from Ni²⁺ can be expressed according to the following reaction:³⁶



where, two Ni²⁺ ions (Ni_{Ni}^x) react with oxygen gas, then create two Ni³⁺ ions (Ni_{Ni}^{*}) and ionized nickel vacancy (V''_{Ni}). The created nickel vacancy and Ni³⁺ ions in the NiO crystal serve as hole acceptors.³⁶ Fig. 2 shows the XPS spectra of Ni 2p and O 1s. In the Ni 2p_{3/2} XPS spectra of both thermal-NiO_x and spin-NiO_x, three peaks are observed, which are located at binding energies of 853.5 eV, 854.5 eV and 855.8 eV. These peaks correspond to the Ni²⁺, nickel-oxyhydroxide (NiOOH), and Ni³⁺, respectively. The reason for the NiOOH peak being observed at 854.5 eV, is that the surfaces of both of the samples were hydroxylated, due to atmospheric exposure. The integrated peak area ratio of Ni³⁺/Ni²⁺ in the NiO_x films calculated from XPS data was equal to 0.69 for both the thermal-NiO_x and spin-NiO_x. In the oxygen O 1s spectra, the peaks located at 529.1 eV, 530.8 eV and 531.5 eV correspond to oxygen, NiOOH, and water, respectively. The peak area corresponding to the NiOOH of spin-NiO_x is larger than that of thermal-NiO_x, because the solution process is exposed to more moisture and air than the vacuum process. This result is consistent with the tendency that spin-NiO_x has better wettability for perovskite solution, shown in Fig. S2.† But when NiOOH is formed on the surface of a NiO_x thin film, the stability and conductivity may be decreased: therefore, it is necessary to control NiOOH on the surface of NiO_x thin film.^{37,38} XPS analysis results indicate that stability and conduction properties of thermal-NiO_x are better than spin-NiO_x, because the integrated peak area ratios of Ni³⁺/Ni²⁺ of both samples are the same, but spin-NiO_x contain more amount of NiOOH.

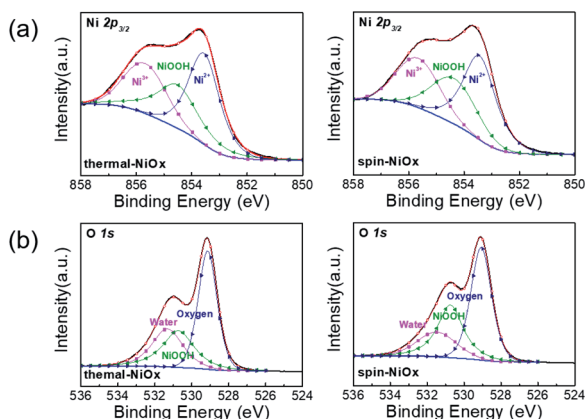


Fig. 2 XPS spectrum of (a) Ni 2p peaks and (b) O 1s peaks of the NiO_x thin film by thermal evaporation and spin coating.

3.2 Energy band alignment of NiO_x thin films for HTL

Fig. 3(a) shows the absorbance and transmittance of NiO_x thin films that were measured by UV/Vis spectroscopy. The transmittance of thermal-NiO_x was slightly higher than that of spin-NiO_x, because the thickness of thermal-NiO_x is thinner than that of spin-NiO_x. The optical energy band gap is calculated using the equation shown below:

$$\alpha h\nu = A(h\nu - E_{\text{gap}})^{1/2} \quad (2)$$

where α , $h\nu$, E_{gap} and A are the absorption coefficient, incident photon energy, optical energy band gap, and constant, respectively.

The calculated energy band gap values of thermal-NiO_x and spin-NiO_x are 3.88 eV and 3.89 eV respectively, and the values are very similar. The ultraviolet photoelectron spectroscopy (UPS) measurement was conducted to analyze the properties of the energy band of NiO_x as shown Fig. 3(b). Although there was no noticeable difference in the highest occupied molecular orbital (HOMO), thermal-NiO_x showed a slightly lower HOMO than spin-NiO_x. Since V_{oc} increases when HTL with deeper HOMO levels are applied to PSCs,^{10,39-41} it is anticipated that the perovskite device with thermal-NiO_x applied has a slightly higher V_{oc} .

3.3 Surface morphologies and microstructures

The surface morphologies of NiO_x thin film and perovskite layer were investigated by scanning electron microscopy (SEM) and

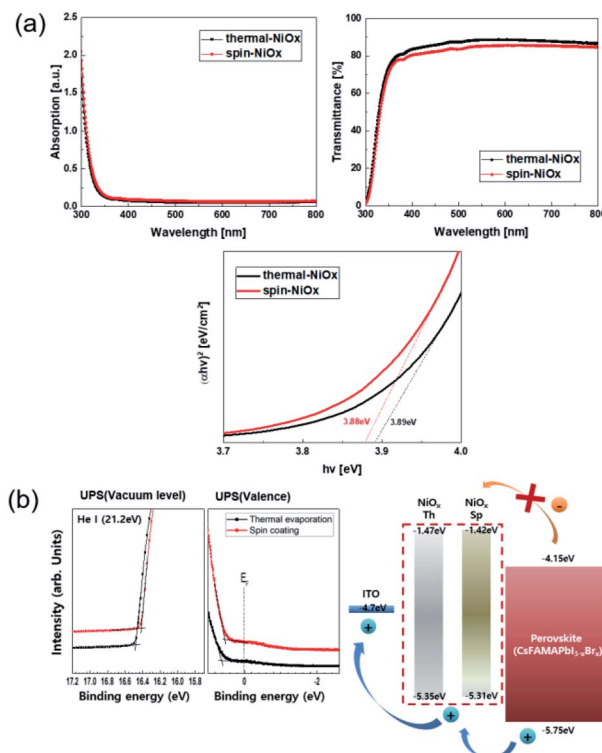


Fig. 3 (a) Absorbance and transmittance of thermal-NiO_x and spin-NiO_x thin film deposited on the glass. And optical energy bandgap of thermal-NiO_x and spin-NiO_x. (b) UPS (He I) spectra and schematic illustration of energy band levels of NiO_x with different coating processes.

atomic force microscope (AFM). Fig. 4(a) shows that compared to the surface morphology of spin-NiO_x, thermal-NiO_x is denser, and has smaller grain size. The grain size of thermal-NiO_x is about 25 nm, but the spin-NiO_x is approximately 50 nm, twice the size of thermal-NiO_x. However, the perovskite layer, coated on the NiO_x thin films deposited by different processes, shows a similar surface morphology regardless of the NiO_x deposition process, and the grain size is about 200–250 nm. Fig. 4(b) shows the surface morphology image measured by AFM. Spin-NiO_x has a rougher surface than thermal-NiO_x. The root mean square (RMS) and actual surface area value were calculated through the AFM results. The RMS value of spin-NiO_x is 3.29 nm, which is about twice that of the thermal-NiO_x (RMS 1.74 nm), and spin-NiO_x has a large actual surface area in the same project area. The actual surface area of the spin-NiO_x was 1.12 μm² and that of the thermal-NiO_x was 1.00 μm² per project area (1.00 μm²). Therefore, it is estimated that when NiO_x is deposited by spin-coating process using nanoparticles, it has a larger contact area with the perovskite layer. The large contact area between the perovskite layer and HTL reduces charge recombination, and contributes to efficient charge carrier transport.^{42,43} In contrast, NiOOH present in a large surface area may adversely affect hole transport.

To compare the microstructures and interface of thermal-NiO_x and spin-NiO_x, high resolution transmission electron

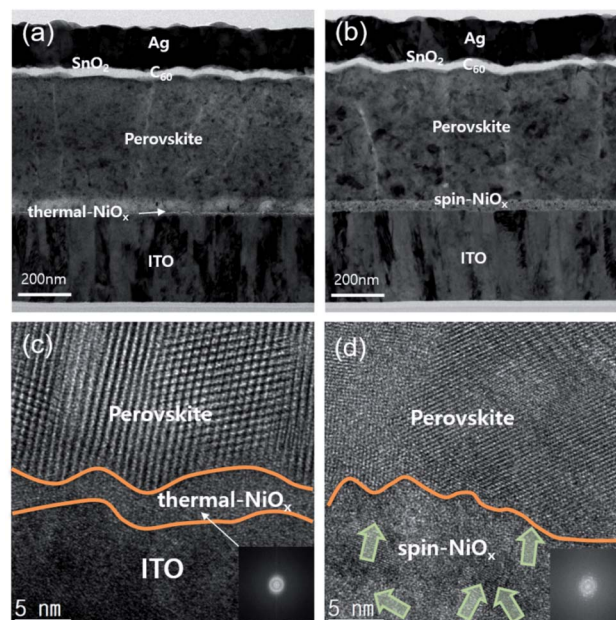


Fig. 5 Cross-sectional TEM image obtained from perovskite solar cell with (a) the thermal-NiO_x HTL, (b) the spin-NiO_x HTL. And enlarged HR-TEM images obtained from (c) interface between thermal-NiO_x and the perovskite active layer, and interface between ITO and thermal-NiO_x, (d) interface between spin-NiO_x and perovskite active layer.

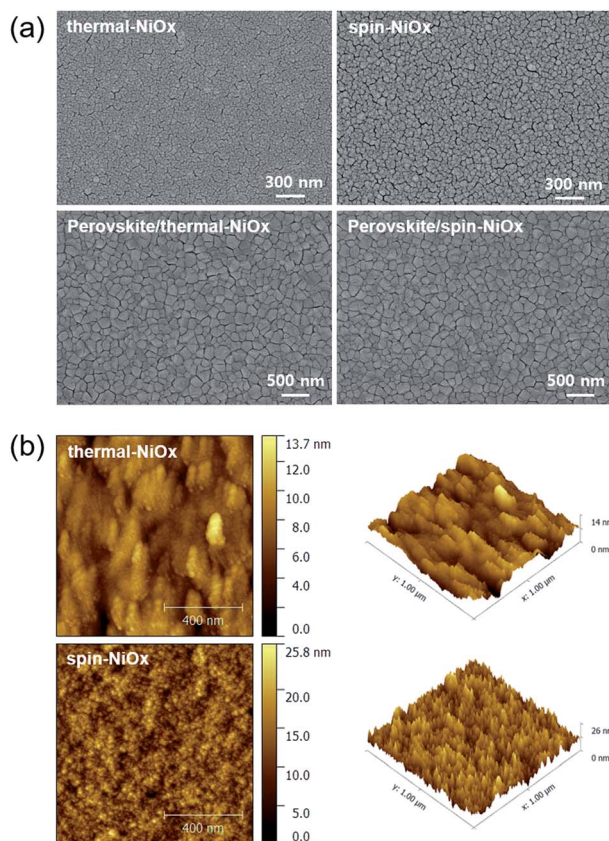


Fig. 4 Comparison between thermal-NiO_x and spin-NiO_x morphologies: (a) SEM images of NiO_x and perovskite deposited on NiO_x, (b) surface image measured by AFM of NiO_x deposited using different deposition processes.

microscopy (HR-TEM) was performed and Fig. 5 shows the measured image. Fig. 5(a) and (b) are cross-sectional TEM images of the inverted-planar PSCs with thermal-NiO_x or spin-NiO_x HTL. All interlayer interfaces of PSCs were well distinguished, and no diffusion at the interface was observed. Fig. 5(c) is enlarged HR-TEM images from the interface between the thermal-NiO_x and the perovskite layer. Fig. 5(c) reveals that the crystallization of NiO_x has not occurred, since the thickness of thermal-NiO_x is very thin (about 5 nm). The diffuse fast Fourier transform (FFT) pattern also confirms the amorphous structure of thermal-NiO_x. On the other hand, Fig. 5(d) shows that spin-NiO_x consists of nanoparticles grown in random directions and there is a well-defined interface between NiO_x and the perovskite layer, without diffusion at the interface. Meanwhile, thermal-NiO_x has a smoother interface with perovskite than the spin-NiO_x which is consistent with the AFM results.

3.4 Performance of the PSCs contained NiO_x HTL

Fig. 6(a) shows the structure of the device that was fabricated to confirm the photoelectric conversion characteristics of the PSC that was applied with NiO_x as HTL. And Fig. 6(a) shows the *J*-*V* curves of the best performing PSC with each of the thermal-NiO_x and spin-NiO_x. The best power conversion efficiency (PCE) of PSCs with thermal-NiO_x was 16.64% (with *V*_{oc} = 1.07 V, *J*_{sc} = 20.68 mA cm⁻² and FF = 75.51%), and that with spin-NiO_x was 16.02% (with *V*_{oc} = 1.02 V, *J*_{sc} = 21.14 mA cm⁻² and FF = 74.14%). Forward and reverse *J*-*V* curves of thermal-NiO_x and spin-NiO_x were shown in Fig. S3.† PSCs with thermal-NiO_x showed little hysteresis, but that with spin-NiO_x showed



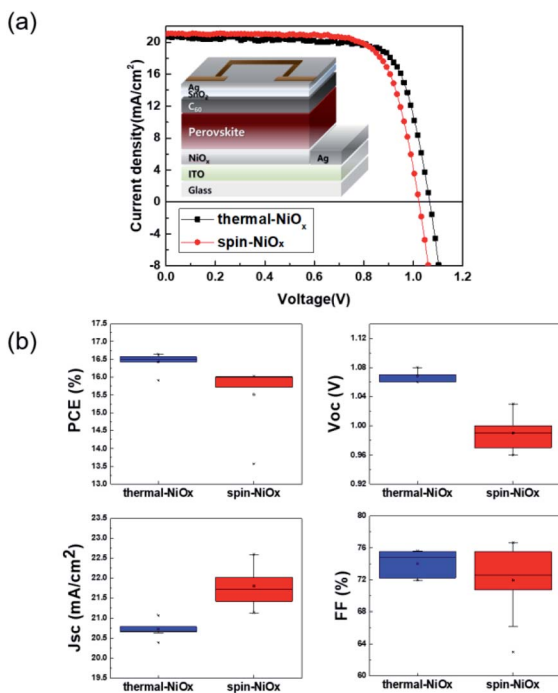


Fig. 6 (a) Current density–voltage curves and schematics of perovskite solar cell with NiO_x for hole transport layer, (b) box chart representation of photovoltaic parameters of perovskite solar cells.

changes in V_{oc} and FF. It is estimated that because spin- NiO_x is less stable due to contain more NiOOH than thermal- NiO_x , as shown in the XPS data. Fig. 6(b) is a box plot showing the distribution of each parameter obtained from the measurement of numerous J – V curves of the PSCs. The average photovoltaic parameter value of PSCs with thermal- NiO_x was $\text{PCE} = 16.43\%$, $V_{oc} = 1.07 \text{ V}$, $J_{sc} = 20.73 \text{ mA cm}^{-2}$ and $\text{FF} = 74.00\%$, whereas that with spin- NiO_x was $\text{PCE} = 15.51\%$, $V_{oc} = 0.99 \text{ V}$, $J_{sc} = 21.80 \text{ mA cm}^{-2}$ and $\text{FF} = 75.51\%$. The V_{oc} of PSC using thermal- NiO_x was higher than that with spin- NiO_x , which is presumed to be because the HOMO level of thermal- NiO_x has a deeper value than that of spin- NiO_x , as shown in Fig. 3(b). In contrast, J_{sc} of PSCs using spin- NiO_x was higher than that using thermal- NiO_x . It is assumed to be because the perovskite layer of PSC with spin- NiO_x is exposed to large amount of light than that of PSC with thermal NiO_x , as shown in Fig. S4†. Fig. S4† shows the optical transmittance spectra of spin- $\text{NiO}_x/\text{ITO}/\text{glass}$, thermal- $\text{NiO}_x/\text{ITO}/\text{glass}$, and ITO/glass , and the transmittance values are 75.7%, 74.2%, and 77.4% respectively in 300 nm–800 nm. The PCE was higher for PSCs including thermal- NiO_x , and all parameters of spin- NiO_x have a wider distribution than those of thermal- NiO_x . The results show that the thermal evaporation process is advantageous for obtaining a thin film with higher reproducibility than the spin-coating process.

4 Conclusions

In summary, we compared a thermal evaporated NiO_x and spin-coated NiO_x to apply the hole transport layers of PSCs. We evaluated the chemical states, energy band alignments, surface

morphologies, and microstructure properties of thermal- NiO_x and spin- NiO_x thin film. While the chemical states and energy band gaps of thermal- NiO_x and spin- NiO_x were not significantly different, thermal- NiO_x had a slightly deeper HOMO level than did spin- NiO_x . But the surface morphologies are different between thermal- NiO_x and spin- NiO_x with the grain size and RMS of spin- NiO_x being about twice as large as that of thermal- NiO_x , and the contact area with perovskite layer also being larger. To evaluate the characteristics for HTL, PSCs were fabricated with thermal- NiO_x or spin- NiO_x and the photovoltaic parameters measured. The PCE of PSCs with thermal- NiO_x was higher than that with spin- NiO_x and the reproducibility was better. Consequently, we confirmed the performance as HTL of NiO_x that was deposited by the thermal evaporation process, and confirmed that the thermal evaporation process is more reproducible than the solution process. Therefore, the thermal evaporation processed NiO_x HTL enables large-scale, economic, and reliable fabrication for next generation.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 Y. Rong, Y. Hu, A. Mei, H. Tan, M. I. Saidaminov, S. I. Seok, M. D. McGehee, E. H. Sargent and H. Han, *Science*, 2018, **361**, 1214.
- 2 H. J. Seok, Y. J. Kang, J. K. Kim, D. H. Kim, S. B. Heo, S. J. Kang and H.-Ki Kim, *Sci. Technol. Adv. Mater.*, 2019, **20**, 1118.
- 3 J. H. Lee, D. G. Lee, H. S. Jung, H. H. Lee and H. K. Kim, *J. Alloys Compd.*, 2020, **845**, 155531.
- 4 H. J. Seok, A. Ali, J. H. Seo, H. H. Lee, N. E. Jung, Y. J. Yi and H. K. Kim, *Sci. Technol. Adv. Mater.*, 2019, **20**, 389.
- 5 M. Zhang, Q. Chen, R. Xue, Y. Zhan, C. Wang, J. Lai, J. Yang, H. Lin, J. Yao, Y. Li, L. Chen and Y. Li, *Nat. Commun.*, 2019, **10**, 4593.
- 6 J. G. Kim, J. H. Lee, S. I. Na, H. H. Lee, Y. S. Kim and H. K. Kim, *Org. Electron.*, 2020, **78**, 105560.
- 7 N. J. Jeon, J. H. Noh, W. S. Yang, Y. C. Kim, S. C. Ryu, J. W. Seo and S. I. Seok, *Nature*, 2015, **517**, 476.
- 8 W. Xiang and W. Tress, *Adv. Mater.*, 2019, **31**, 1902851.
- 9 M. I. Asghar, J. Zhang, H. Wang and P. D. Lund, *Renewable Sustainable Energy Rev.*, 2017, **77**, 131.
- 10 Y. Shao, Y. Yuan and J. Huang, *Nat. Energy*, 2016, **1**, 15001.
- 11 A. Dubey, N. Adhikari, S. Mabrouk, F. Wu, K. Chen, S. Yang and Q. Qiao, *J. Mater. Chem. A*, 2018, **6**, 2406.
- 12 K. P. Bhandari and R. J. Ellingson, *A Comprehensive Guide To Solar Energy Systems*, Academic Press, Cambridge, 2018, p. 233.



- 13 Z. Song, S. C. Waththage, A. B. Phillips and M. J. Heben, *J. Photonics Energy*, 2016, **6**, 022001.
- 14 K. D. M. Rao and G. U. Kulkarni, *Nanoscale*, 2014, **6**, 5645.
- 15 J. K. Kim, D. N. Nguyen, J. H. Lee, S. H. Kang, Y. S. Kim, S. S. Kim and H. K. Kim, *J. Alloys Compd.*, 2020, **818**, 152887.
- 16 S. Nair, S. B. Patel and J. V. Gohel, *Mater. Today Energy*, 2020, **17**, 100449.
- 17 R. Wang, M. Mujahid, Y. Duan, Z. K. Wang, J. Xue and Y. Yang, *Adv. Funct. Mater.*, 2019, **29**, 1808843.
- 18 L. Meng, J. You, T. F. Guo and Y. Yang, *Acc. Chem. Res.*, 2016, **49**, 155.
- 19 L. Calió, S. Kazim, M. Grätzel and S. Ahmad, *Angew. Chem., Int. Ed.*, 2016, **55**, 14522.
- 20 J. H. Kim, P. W. Liang, S. T. Williams, N. C. Cho, C. C. Chueh, M. S. Glaz, D. S. Ginger and A. K. Y. Jen, *Adv. Mater.*, 2014, **27**, 695.
- 21 U. S. Kwon, B. G. Kim, D. C. Nguyen, J. H. Park, N. Y. Ha, S. J. Kim, S. H. Ko, S. I. Lee, D. H. Lee and H. J. Park, *Sci. Rep.*, 2016, **6**, 30759.
- 22 Z. Zhu, Y. Bai, T. Zhang, Z. Liu, X. Long, Z. Wei, Z. Wang, L. Zhang, J. Wang, F. Yan and S. Yang, *Angew. Chem., Int. Ed.*, 2014, **53**, 12571.
- 23 K. C. Wang, P. S. Shen, M. H. Li, S. Chen, M. W. Lin, P. Chen and T. F. Guo, *ACS Appl. Mater. Interfaces*, 2014, **6**, 11851.
- 24 J. H. Park, J. W. Seo, S. M. Park, S. S. Shin, Y. C. Kim, N. J. Jeon, H. W. Shin, T. K. Ahn, J. H. Noh, S. C. Yoon, C. S. Hwang and S. I. Seok, *Adv. Mater.*, 2015, **27**, 4013.
- 25 T. Abzieher, S. Moghadamzadeh, F. Schackmar, H. Eggers, F. Sutterlütli, A. Farooq, D. Kojda, K. Habicht, R. I. Schmäger, A. Mertens, R. Azmi, L. Klotz, J. A. Schwenzer, M. Hetterich, U. Lemmer, B. S. Richards, M. Powalla and U. W. Paetzold, *Adv. Energy Mater.*, 2019, **9**, 1802995.
- 26 Z. Liu, A. Zhu, F. Cai, L. Tao, Y. Zhou, Z. Zhao, Q. Chen, Y. Cheng and H. Zhou, *Royal Society of Chemistry*, 2017, **5**, 6597.
- 27 S. R. Pae, S. G. Byun, J. K. Kim, M. K. Kim, I. Gereige and B. H. Shin, *ACS Appl. Mater. Interfaces*, 2018, **10**, 534.
- 28 V. Manjunath, S. Bimli, K. H. Parmar, P. M. Shirage and R. S. Devan, *Sol. Energy*, 2019, **193**, 387.
- 29 H. N. Lee and B. J. Song, *J. Korea Acad. Industr. Coop. Soc.*, 2011, **12**, 2267.
- 30 W. Chen, Y. Wu, Y. Yue, J. Liu, W. Zhang, X. Yang, H. Chen, E. Bi, I. Ashraf, M. Grätzel and L. Han, *Science*, 2015, **350**, 944.
- 31 H. Sato, T. Minami, S. Takata and T. Yamada, *Thin Solid Films*, 1993, **236**, 27.
- 32 D. S. Kim and H. C. Lee, *J. Appl. Phys.*, 2012, **112**, 034504.
- 33 N. Kumar, H. B. Lee, S. B. Hwang and J. W. Kang, *J. Mater. Chem. A*, 2020, **8**, 3357.
- 34 W. Yu, L. Shen, S. Ruan, F. Meng, J. Wang, E. Zhang and W. Chen, *Sol. Energy Mater. Sol. Cells*, 2012, **98**, 212.
- 35 W. Chen, Y. Wu, J. Fan, A. B. Djurišić, F. Liu, H. W. Tam, A. Ng, C. Surya, W. K. Chan, D. Wang and Z. B. He, *Adv. Energy Mater.*, 2018, **8**, 1703519.
- 36 W. L. Jang, Y. M. Lu, W. S. Hwang, T. L. Hsiung and H. P. Wang, *Appl. Phys. Lett.*, 2009, **94**, 062103.
- 37 S. Liu, S. Ho, Y. Chen and F. So, *Chem. Mater.*, 2015, **27**, 2532.
- 38 S. R. Seo, I. J. Park, M. J. Kim, S. H. Lee, C. D. Bae, H. S. Jung, N. G. Park, J. Y. Kim and H. J. Shin, *Nanoscale*, 2016, **8**, 11403.
- 39 S. Chen, Y. Hou, H. Chen, M. Richter, F. Guo, S. Kahmann, X. Tang, T. Stubhan, H. Zhang, N. Li, N. Gasparini, C. O. R. Quiroz, L. S. Khanzada, G. J. Matt, A. Osvet and C. J. Brabec, *Adv. Energy Mater.*, 2016, **6**, 1600132.
- 40 N. G. Park and W. Tress, *Organic-Inorganic Halide Perovskite Photovoltaics*, Springer, New-York, 2016.
- 41 Z. H. Bakr, Q. Wali, A. Fakharuddin, L. Schmidt-Mende, T. M. Brown and R. Jose, *Nano Energy*, 2017, **34**, 271.
- 42 Z. Jin, Y. Guo, S. Yuan, J. S. Zhao, X. M. Liang, Y. Qin, J. P. Zhang and X. C. Ai, *Royal Society of Chemistry*, 2020, **10**, 12289.
- 43 S. Ma, T. Ye, T. Wu, Z. Wang, Z. Wang, S. Ramakrishna, C. Vijila and L. Wei, *Sol. Energy Mater. Sol. Cells*, 2019, **191**, 389.

