Nickel Oxide for Perovskite Photovoltaic Cells

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Organic–inorganic perovskite solar cells (PSCs) have shown tremendous progress from 3.8% power conversion efficiency (PCE) in 2003 to 25.2% in 2020 because of their wide range of light absorption, fast charge separation, long carrier diffusion length, and long carrier lifetime. The optoelectronic characteristics of hole transport material (HTM) and electron transport material (ETM) strongly affect photovoltaic (PV) performance and stability of PSCs. Recently, various inorganic HTMs with high efficiency, stability, and cost-effectiveness have been investigated. Among them, nickel oxide (NiOx) is one of the most studied inorganic HTMs in terms of device performance and stability because it has high hole mobility, electrical conductivity, transmittance, and energetically favorable band alignment, along with environmental stability. This article overviews the recent progress on NiOx-based planar PSCs. The main focus is on the structural, electrical and optical properties of the NiOx thin film, which mainly depends on the synthesis methods and post-treatments. Firstly, a variety of methods are investigated to fabricate dense, compact and high crystallized NiOx thin film. Moreover, multifarious doping strategies and surface functionalization using organic materials are summarized as approaches to improve their properties for realizing high performance p–i–n planar PSC devices.

1. Introduction

With a rapid increase in population and industrialization, annual energy consumption is predicted to be about 30 TW in 2050, which is almost double compared with the consumption of 2015.[1] Although the usage of fossil fuel has propelled our welfare and quality of life as a primary energy source, it exacts a huge penalty on humankind as well as the environment. Due to regular usage of fossil fuels, it has been dwindling. To address these issues, extremely urgent efforts are being mobilized to identify the potential alternate energy sources that should be renewable, ecofriendly, and inexpensive. Solar energy represents one of the most abundant renewable energy sources, available to the human being. Indeed, 1 h of solar flux arriving to our planet is just enough for global energy consumption over a year.[2] However, the contemporary challenges are to identify the viable systems for harvesting, transporting, and storing the solar energy in an efficient manner. The current photovoltaic (PV) electricity generation is completely dominated by the crystalline silicon solar cell due to its fairly high power conversion efficiency (PCE) of >26% with reasonable manufacturing cost.[3] However, its rigidity, originated from its indirect bandgap, limits its utilization except in solar power plants and rooftop PV systems. As alternatives, the second-generation solar cells such as CdTe and CIGS solar cells have been developed,[4] and more importantly, third-generation solar cells like organic PVs, dye-sensitized solar cells (DSSCs), and quantum dot PV cells that can be fabricated by simple process techniques on low-cost unconventional substrates have shown tremendous advancement in their reproducibility and stability.[5] However, their PCEs are still lagging behind the conventional silicon solar cells.

In this situation, the advent of perovskite solar cells (PSCs) in 2009 has revolutionized the third-generation solar cells due to its spectacular improvement in efficiency from 3.9% to 25% in a decade,[6] along with its ease of fabrication methods that can be extended to a low-cost roll-roll process. In general, the organic–inorganic mixed-halide perovskites ABX3 (A site: methyl ammonium (CH3NH3+) or formamidinium (CH3NH2)+ with a mixture of Cs+ or Rb+, B site: Pb2+ or Sn2+, and X site: Cl-, Br-, or I-) have been utilized as photoactive light absorbers due to their excellent optoelectronic properties such as high light absorption coefficient (105 cm-1), small exciton binding energy, convenient bandgap tunability, large charge carrier diffusion length (>1 µm), and fairly high defects tolerance capacity.[7] In addition to these, these superior optoelectronic properties, perovskites have good flexibility in the design of device architecture and configuration. In general, PSCs can be classified into two basic structures, as regular (n–i–p) and inverted (p–i–n) structures, which depend on the position of electron transport layer (ETL) and
hole transport layer (HTL) on the exterior portion of the cell confronted by incident light first.\textsuperscript{[9]} Further, it can also be divided into two categories, mesoporous and planar structures. In the mesoporous PSCs, the mesoporous TiO\textsubscript{2} scaffold layer is usually incorporated between the perovskite and ETL layer,\textsuperscript{[10]} which is analogous to the solid-state DSSCs. The high PCE of 25.5% with a regular architecture was attained, in which mesoporous TiO\textsubscript{2} acted as the ETL.\textsuperscript{[6]} However, the mesoporous ETL requires high-temperature annealing, which restricts the compatibility with flexible and tandem PSC applications. Moreover, the mesoporous layer with a thickness greater than 150 nm showed ineffective electron transport property due to its high surface roughness.\textsuperscript{[10]} As such, it is ideal to fabricate thin mesoporous ETLs although this is challenging. These limitations led to the emergence of the simplified planar configurations of PSCs (planar n-i-p and p-i-n).

As a general tendency, the regular-type (n-i-p) PSCs, which use crystalline ETLs (TiO\textsubscript{2}, SnO\textsubscript{2}, ZnO, etc.), have shown high efficiency compared with that of inverted-type (p-i-n) PSCs, and the superior stability of those ETLs provides a large process window to the following solution-based perovskite layer formation (e.g., solvent, processing temperature, etc.).\textsuperscript{[11]} Nevertheless, inverted-type PSCs, which resemble the structures of organic PV cells, are also under the spotlight, due to their advantages such as low-temperature processibility suitable for the processing of flexible devices.\textsuperscript{[12]} It has been widely known that ETL and HTL play a crucial role to achieve better performance in PSCs, and various efforts have been conducted to modify the ETL and HTL.\textsuperscript{[13]–[16]} As for the ETL, various types of stable inorganic semiconductors are available, but, most hole transport materials (HTM) have an organic nature, are less stable as they are easily degraded by water and oxygen, and reduce device stability as well as efficiency. Hence, there is an urgent need to develop more efficient inorganic HTMs.

The ideal HTM should possess the following characteristics such as 1) better energy-level alignment with perovskite (i.e., highest occupied molecular orbital (HOMO) level of HTM is well matched with the valence band of the perovskite), which promotes the extraction of holes from the perovskite and reduces their recombination at the interface. 2) high hole mobility, which facilitates the transportation of hole carriers, 3) high chemical and thermal stability, and 4) facile processibility with low production cost and a simple preparation procedure, which are more applicable to future large-scale applications.\textsuperscript{[17]} The varieties of organic materials have been developed as HTMs in n-i-p and p-i-n configurations of PSCs. Among these, the small-molecule-based 2, 2', 7', 7'-tetrakis (N,N-di-p-methoxyphenylamine)-9, 9'-spirobifluorene (spiro-OMeTAD) has been one of the most widely used HTMs so far, which exhibited a PCE over 23% in planar PSCs.\textsuperscript{[18]} However, low hole mobility, amorphous nature, and tedious synthesis procedure additionally require p-type dopants (i.e., FK209), and high cost limits its further usage. In contrast, the organic polymer-based poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) has been also widely used as a HTM in inverted PSCs.\textsuperscript{[19]} However, its work function, unmatched with the valence band of perovskite, poor stability, and high preparation cost constrain its further extension to a large-scale practical application. Therefore, considerable research activities in this field have been dedicated to the exploration of alternative low-cost and efficient inorganic HTMs in PSCs.\textsuperscript{[20]}

So far, various inorganic HTMs such as CuSCN, CuI, Cu\textsubscript{2}O, CuS, CuGaO\textsubscript{2}, CuAlO\textsubscript{2}, NiO\textsubscript{x}, MoO\textsubscript{3}, and MoS\textsubscript{2} have been used as HTLs in PSCs.\textsuperscript{[21]–[30]} Among these, NiO\textsubscript{x} is one of the most promising low-cost HTMs. Nickel oxide has a cubic structure with Fm3m space group similar to NaCl, and the corresponding lattice parameter is 0.4173 nm. Pure stoichiometric NiO behaves as an insulator at room temperature and its electrical conductivity is just less than 10\textsuperscript{−11} S cm\textsuperscript{−1}.\textsuperscript{[31]} However, due to the presence of NiO\textsubscript{2}H and NiO\textsubscript{3}, excess amount of oxygen is always observed in practice, and those induce the nonstoichiometric state, represented as NiO\textsubscript{x}. Excess amount of oxygen leads to Ni vacancies and thus holes are created, which provide a p-type characteristic to NiO\textsubscript{x}.\textsuperscript{[32]} Optoelectronic properties of NiO\textsubscript{x} are highly sensible with the Ni and O stoichiometry, and this can be tuned by processing conditions. For example, it has been reported that the stoichiometry of the as-deposited film, to be NiO\textsubscript{1.96±0.10}, ensuring around 90% of Ni(OH)\textsubscript{2} along with 10% of NiO, can be changed to be NiO\textsubscript{1.07±0.16} and NiO\textsubscript{1.17±0.12} at 200 and 400 °C, respectively.\textsuperscript{[33]} A nonstoichiometric NiO\textsubscript{x} film, synthesized by a chemical precipitation method, showed an atomic ratio of Ni:O to be 1:1.14, in which NiO\textsubscript{OH}, NiO\textsubscript{2}, and NiO coexisted with 1.13:1:22.1 ratio, and its composition and its related work function, affecting the performances of solar cells, were shown to be changed over 200 °C annealing temperature.\textsuperscript{[34]}

NiO\textsubscript{x} has numerous merits, including excellent visible transparency with a wide bandgap (>3.5 eV), a deep lying valence band maximum (VBM) (E\textsubscript{VBM}: 5.2 eV), superior chemical, thermal, and light stability, and compatibility with low-temperature processes, feasible for flexible substrates.\textsuperscript{[35]} The p-i-n PSCs, built on various types of NiO\textsubscript{x} layers (e.g., solution-based processes and vacuum-assisted depositions), have shown promising performances with negligible hysteresis and long-term stability.\textsuperscript{[36–38]} However, their low intrinsic conductivity (<10\textsuperscript{−4} S cm\textsuperscript{−1}) and their surface defects, which were especially pin holes and island morphology, have been long-standing issues to resolve.\textsuperscript{[31]} Furthermore, a relatively distinct energy gap between their Fermi level and VBM can induce a large energy-level offset at the interface between NiO\textsubscript{x} and perovskite.\textsuperscript{[39–46]} In this Review, we will discuss the strategies to overcome these drawbacks by enhancing their properties, including their synthetic routes, extrinsic doping processes, and modifications for defect passivation. Finally, the challenges and future outlooks for further improving the performance and stability of NiO\textsubscript{x}-based PSCs will be discussed.

2. Synthetic Methods of NiO\textsubscript{x}

Energy bands of HTMs for PSC devices are shown in Figure 1, for reference. Among those, the approaches, based on NiO\textsubscript{x} and its derivatives, for p-i-n-structured PSCs, are main the focus of this Review. The properties of NiO\textsubscript{x} thin films are largely affected by their synthetic methods including process conditions, because every synthesis method provides different concentrations of Ni\textsuperscript{2+} and Ni\textsuperscript{3+} valence states on the thin film, and its morphology can be significantly affected by the methods. These properties lead to the variation of PV performances of PSCs. In this section, we
summarize those methods, developed to synthesize high-quality NiO$_x$ thin film (Figure 2), and their impacts on the film properties and PV performance are discussed.

### 2.1. Solvothermal Synthesis

The solvothermal method has been widely utilized for the synthesis of NiO$_x$ nanocrystals. This method has easy processibility, and the distribution of particle size and shape including its crystallinity can be precisely controlled. NiO$_x$ nanoparticles (NPs), synthesized by this method, are already in the crystalline form, and therefore the high-temperature annealing process can be often skipped after spin casting,[47,48] but low-temperature post-annealing is usually required to remove the residual organic solvent, remaining on the surface.

The synthesized NiO$_x$ NP powder can be easily dissolved in solvents such as deionized water, isopropyl alcohol, etc, and the spin-casting process is frequently utilized to obtain a high-quality NiO$_x$ film, in the range of nanometer-to-micrometer thickness, with the crystallized nanocrystals. In the spin-cast process, the substrate is kept on a chuck and rotates at the desired speed after the solution’s dropping. The centrifugal force puts the solution outward, but the viscosity and surface tension help the growth of a uniform thin film. Finally, the thin film is heated at the desired temperature to remove organic contamination, and an additional high-temperature annealing can further enhance the crystallinity and grain size of NiO$_x$ layer, affecting its morphology and the performances of PV cells built on the layer. The schematic representation of spin casting is shown in Figure 3a. Because the spin-cast NiO$_x$ NPs can be annealed at low temperatures, various substrates can be utilized. However, this method significantly depends on the NiO$_x$ NPs’ quality, which requires the optimization of the synthesis platform. In addition, synthesizing NiO$_x$ NP powder requires a lot of steps and time compared with other approaches. The surface morphology of NiO$_x$ thin film is also significantly dependent on the quality of solution as well as the rotation speed, and thus dissolving NiO$_x$ nanocrystals into the solvent is crucial. This affects the morphology of NiO$_x$ film and finally the performance of the device.[37,49,50] The high quality of HTL improves the morphology of the following perovskite layer and reduces the nonradiative recombination at the interface between HTL and photoactive layer.

Generally, NiO$_x$ NPs can be prepared by thermally decomposing Ni(OH)$_2$ in a furnace. Ni(OH)$_2$ is synthesized by the reaction of nickel(II) nitrate hexahydrate(or nickel(II) chloride hexahydrate) with NaOH in DI water-based conditions (around pH 10).[51,52] The NPs synthesized by this method have an average size $\approx$10 nm, and the prepared NiO$_x$ thin film has rough morphology along with moderate density. The solar cell fabricated on the NiO$_x$ film obtained by this method showed efficiency at around 17%,[53–55] and it could be further enhanced up to 18.6% by the modifications of the absorber layer and the interface.[54] This approach is convenient for the fabrication of flexible solar cells.[53,54]
Recently, high-quality NiO\(_x\) NPs were synthesized using stable ink in ethanol. The scanning electron microscopy (SEM) image ensured that the ethanol-dispersed NiO\(_x\) NPs covered the whole surface, as shown in Figure 3b. Moreover, the atomic force microscopy (AFM) image confirmed the smoothness of film, and its roughness was found at around 5.3 nm (Figure 3c). High-intense peaks of X-ray diffraction (XRD) patterns in Figure 3d validated the high crystallinity of the NiO\(_x\) film. Fourier-transform infrared spectroscopy (FTIR) characterization was also conducted to examine the formation of chemical bonds on the surface of NiO\(_x\) films (Figure 3e). No peaks were observed in the ethanol-dissolved NiO\(_x\) NPs, which confirmed the ligand-free behavior, whereas various peaks corresponding to water, hydroxyl groups, and other functional ligands on the surface were found from the water-dissolved NPs. J–V curves of rigid and flexible W/E-NiO\(_x\)-based perovskite PV cells showed 18.49% and 15.89% PCEs, respectively (Figure 3f,g).[57] The PSC, built on the ethanol-dissolved NiO\(_x\) NPs, retained 90% of initial efficiency after the 500 h, whereas the PSC device, prepared on water-dissolved NiO\(_x\) NPs, reduced to 40% of its initial efficiency, as shown in Figure 3h.

2.2. Sol–Gel Method

The sol–gel method is most frequently used to deposit the NiO\(_x\) films, due to its simplicity and good reliability. This method has advantages, such as low energy consumption and easy incorporation of atoms due to molecular-level mixing, but it has disadvantages like long processing time and difficulty in removal of hydroxyl and carbon groups. High-temperature annealing is another disadvantage preventing its industrial scale production. In this method, the metal precursors, usually utilized as stabilizing agents, are dissolved in the organic solvent. This solution is further used for the deposition of film using spin casting or spray...
pyrolysis. As for the spin-cast films, those thin films should be annealed at a high temperature to remove the organic impurity and enhance their crystallinity and grain size. It is also observed that the bandgap is shifted toward lower energy with increasing the annealing temperature. The annealing atmosphere also affects the properties of NiOx films. Zhao et al. synthesized NiOx thin films using a sol−gel method and annealed them in air, O2, N2, and Ar atmosphere. It was shown that the electrical properties of NiOx were modified with these atmospheres due to the formation of point defects. The resistivity values of NiOx films were found in the order of Ar > N2 > air > O2, and higher mobility was observed from the film annealed in O2 and air atmosphere, compared with those annealed in N2 and Ar. High conductivity and mobility are advantageous for fast charge carrier transport, and improved PV performances were confirmed for the PSC devices with NiOx annealed in the oxygen-rich atmosphere, compared with those with NiOx prepared in inert condition.

Meanwhile, for spray pyrolysis, the substrate is often heated at the desire temperature, and crystallization can be affected by the deposition time. A schematic representation of thin-film deposition by the spray-pyrolysis method is shown in Figure 4a. Spray pyrolysis is a simple and inexpensive deposition method, and dense and large-scale NiOx thin film can be obtained. There have been various approaches to prepare the solutions for sol−gel method-based NiOx thin films, and a wide range of PCEs were reported from the planar p−i−n PSCs. The one-step spin-casting process, followed by antisolvent treatment, has been widely used to grow high-quality perovskite films on NiOx thin films, and PCEs close to 15% were reported. When the perovskite film was further heated in the presence of solvent vapor, the crystalline size increased; as a result, the PCE reached 17.64%.

Han and coworkers reported several works on the growth of NiOx layer using the spray-pyrolysis method. The substrate temperature for the spray pyrolysis method was kept at around 500−560 °C, and a similar temperature was used during postannealing to improve film crystallinity. The PSCs, based on the spray-pyrolysis-cast NiOx thin film and ethyl acetate-modified perovskite film, showed efficiency of around 15.58% and the J−V curve and SEM image of the device are shown in Figure 4b,c, respectively. They enhanced the efficiency of devices to around 17.6% over the 1 cm² active area, as shown in Figure 4d, and the SEM of the corresponding device is shown in Figure 4e. The maximum efficiency of PSCs, reported with the spray-pyrolyzed NiOx, was 19.19% (Figure 4f), and the SEM image of the device is shown Figure 4g. The sol−gel method is one of the simplest methods to produce NiOx thin film, but its necessity of high temperature annealing limits its application to the flexible solar cell fabrication. Moreover, additional additives such as stabilizing agent and surfactant for the chemical reaction on the substrate can be factors that reduce the purity of thin films when the annealing process is not conducted enough.

![Schematic representation of spray-pyrolysis method.](image)

**Figure 4.** a) Schematic representation of spray-pyrolysis method. b,d,f) J−V curves of devices using NiOx synthesized by spray pyrolysis. c,e,g) Cross-sectional SEM images of devices corresponding to each (b,d,f). Reproduced with permission. Copyright 2017, WILEY-VCH. Copyright 2016, The Royal Society of Chemistry.
2.3. Combustion Method

The combustion method is a self-propagating high-temperature synthesis method, because the heat, limited in a small quantity of precursors, easily dissipates due to the large surface-to-volume ratio of thin films. Therefore, the substrate is not significantly influenced by heat, and thus flexible plastic substrates can be used. [75,76] Zhang and coworkers deposited the NiO\textsubscript{x} thin film at 175 °C using the combustion method. [77] Jen and coworkers reduced the deposition temperature to 150 °C by replacing glycine with acetylacetone. [78] Hao and coworkers synthesized NiO\textsubscript{x} thin film and compared its properties with the sol–gel method-based thin film. [79] Although the surface morphology and roughness were almost the same (Figure 5b–e), the XRD peaks of the combustion-based thin film were more intense than those of sol–gel-derived thin film, ensuring higher crystallinity of the combustion-based thin film even with its lower processing temperature (Figure 5a). Furthermore, the combustion-based NiO\textsubscript{x} thin film was confirmed to have high transmittance (Figure 5f), and steady-state and time-resolved photoluminescence (PL) results represented efficient charge extraction at the interface between perovskite and combustion-based NiO\textsubscript{x} thin film (Figure 5g,h). The PSC device, built on the combustion-based NiO\textsubscript{x} thin film, showed maximum PCE of 20.2% with high stability and low hysteresis (Figure 5i–k).

Combustion methods can save time and energy compared with other deposition methods. The strength and feature of this method are that it can induce an exothermic reaction based on chemical reaction mechanism without additional heating from outside. However, the major drawback of this method is that the chemical reaction may produce unreacted precursors. Moreover, if the reaction is not controlled uniformly throughout the reaction area, the size distribution of oxide particles will increase, reducing the uniformity of the film. These chemical and structural issues can act as defects in PSCs, and therefore, this method should be optimized by comparing and analyzing the properties of thin films and processing conditions.

Figure 5. a) XRD patterns of FTO substrate, sol–gel, and combustion method-processed NiO\textsubscript{x} films. AFM images of b) sol–gel- and c) combustion-processed NiO\textsubscript{x} thin films. Top-view SEM images of the perovskite films deposited on d) sol–gel- and e) combustion-processed NiO\textsubscript{x} thin films. f) Absorption coefficient as a function of photon energy for sol–gel- and combustion-processed NiO\textsubscript{x} thin films. g) Steady-state PL spectra of perovskite films deposited on the sol–gel- and combustion-processed NiO\textsubscript{x} thin films. h) Time-resolved PL of perovskite films deposited on the sol–gel- and combustion-processed NiO\textsubscript{x} thin films. i) J–V curves of perovskite PV cells based on different HTLs. j) Ambient air stability of unencapsulated perovskite PV cells based on different HTLs. k) J–V curves of perovskite PV cells based on combustion-based NiO\textsubscript{x}. Reproduced with permission. [79] Copyright 2018, WILEY-VCH.
2.4. Electrodeposition

Electrodeposition is a simple and cost-effective method to deposit NiOx films, which have potential for large-scale mass production. Moreover, it has numerous advantages such as low-energy consumption, less safety, and minimum production of byproducts for disposal. The electrodeposition process of NiOx thin film is usually composed of two steps: the first step is the deposition of Ni(OH)2 from nickel precursor, and the second step is annealing Ni(OH)2 thin film at the desired temperature to obtain NiOx thin film.[12,80,81] Nickel nitrate is frequently used as an electrolyte, and nitrate ion is converted to nitrile ion in the presence of H2O, providing hydroxyl ions. The nickel and hydroxyl ions produce nickel hydroxide, and it is deposited on the substrate. Further heating above 300 °C converts it to NiOx. The electrochemical deposition process of NiOx thin film can be explained with the following equation:

\[
\begin{align*}
\text{NO}_3^- + \text{H}_2\text{O} + 2e^- & \rightarrow \text{NO}_2^- + 2\text{OH}^- \\
2\text{OH}^- + \text{Ni}^{2+} & \rightarrow \text{Ni(OH)}_2 \\
\text{Ni(OH)}_2 & \rightarrow \text{NiO} + \text{H}_2\text{O}
\end{align*}
\]

The surface uniformity of NiOx thin films, prepared at different current densities of 0.1, 0.2, and 0.5 mA cm\(^{-2}\), was investigated by AFM and SEM (Figure 6a), and it was further examined by the cross-sectional SEM images (Figure 6b).[81] Those results showed that the surface roughness of the NiOx film decreased from 5.0 to 2.1 nm with the change in current density from 0.1 to 0.5 mA cm\(^{-2}\) (Figure 6c). Figure 6d shows the effect of current density on the surface morphology of NiOx film along with the total number of charges. It was shown that the porous, rougher, and thicker NiOx film, deposited at 0.1 mA cm\(^{-2}\), was beneficial for obtaining PSCs having a high fill factor (FF) without degrading Jsc and Vsc, as shown in Figure 6e.[81] The fabricated device showed a maximum PCE of 17.0% with an active area of 1.084 cm\(^2\) (Figure 6f), and its external quantum efficiency (EQE) signals are shown in Figure 6g.

Electrodeposition is a method that allows uniform and nanostructured thin films to be deposited on a large area by the electrochemical process. Therefore, it is one of the promising methods for the commercialization of PSCs. It can easily adjust the thickness of NiOx thin film by controlling deposition time and applied current. However, its usage on the flexible substrate is restricted due to its high-temperature annealing process. In addition, when the deposition current is low, voids are generated in the film, and they increase the roughness of the film. Those rough films can transpire the undesirable performance of PSCs. Accordingly, optimization of the processing condition is necessary.

2.5. Pulsed Laser Deposition

Despite the advantages of solution-processed NiOx such as low cost and simple processability, they are known to have various defects, degrading light transmittance and carrier transportation characteristics. Pulsed laser deposition (PLD) method has been widely utilized for the deposition of high-quality thin films. This process uses a high-power pulsed laser beam that strikes the target in an ultrahigh vacuum chamber. The targeted material is evaporated to form the plasma plume and then deposited on the substrate. This is a simple reactive deposition process that can maintain the exact stoichiometry of the film with relatively high deposition rates. Due to the ejection of high-energy particles from the target with the help of laser plume, the PLD film has high crystallinity even at a relatively low temperature. The schematic representation of PLD method is shown in Figure 7a. Park et al. synthesized the “nanostructured” NiOx films using this PLD method, and those well-organized NiOx nanostructured thin films, positioned at the bottom of the perovskite, improved PV device performances.[82] As shown in the cross-sectional and top-view SEM images of NiOx films, deposited at different oxygen partial pressures (Figure 7c), their morphology and corresponding properties could be controlled by adjusting the partial oxygen pressure and laser power. The schematic representation of thin-film growth at different oxygen pressures is shown in Figure 7d. Their porosity and roughness increased with the partial oxygen pressure during the process, and thus their transmittance in the visible wavelength range, under the same thickness condition, increased with the oxygen pressure (Figure 7g). However, the “disordered” NiOx thin film having high porosity, prepared at the highest oxygen pressure condition, was not efficient for hole extraction. XRD patterns also showed that its crystallinity and orientation decreased with the oxygen pressure (Figure 7f). At 200 mTorr oxygen pressure, NiOx nanostructure had high crystallinity, oriented along (111) plane, whereas its crystallinity and orientation degraded at higher pressure conditions.

\(J–V\) curves of PSCs with NiOx layers, prepared under different oxygen pressure conditions, are shown in Figure 7e, and a maximum PCE of 17.3% was achieved from the “nanostructured” NiOx films, processed at 200 mTorr oxygen pressure condition (Figure 7b). The enhanced performance in a nanostructured NiOx film was attributed to the slow recombination rate during the extraction and transport of the dissociated carriers. As a result, the (111)-oriented nanostructured NiOx film with good optical transparency played a key role in the efficient extraction of holes and the prevention of electron leakage as an HTM in a PSC. However, the PLD method has some limitations on large-scale growth and conformal coverage, and those have limited the application of the PLD method to the large-scale production of PSCs.

The NiOx thin films, deposited by low-temperature solution processes, have structural defects, and these defects reduce charge carrier extraction and transportation capability of NiOx thin film. In this aspect, the PLD method that can improve the film uniformity and density is highly desirable. Furthermore, it can precisely control the thickness of the film by controlling the deposition parameters (i.e., \(O_2\) partial pressure and deposition time), and it can be processed at low temperatures without direct heat energy, applied to the substrate, promising flexible PSC fabrication. Nevertheless, high energy, required for the direct plasma treatment on a target material, can be a difficulty in depositing the NiOx thin film using this approach. In addition, an expensive equipment to maintain an ultrahigh vacuum condition during the deposition process is needed, and the area and the number of substrates are limited to the chamber size.
2.6. E-Beam Deposition

A schematic representation of e-beam deposition is shown in Figure 8a. When a source material is targeted by a high-energy electron beam, the electron loses their energy, instantly inducing large thermal energy, useful for evaporation. For the NiO\textsubscript{x} thin-film formation, Ni metal is utilized as a source material, and its stoichiometry varies with the annealing temperature and flow rate of oxygen.\cite{36,83} The Ni ion reacts with the oxygen atom, consequently forming NiO\textsubscript{x} at a certain annealing temperature. Figure 8b,c shows SEM images of NiO\textsubscript{x} films, prepared by vacuum-assisted e-beam deposition and solution-based spin coating. Figure 8d shows the schematic of the Ni(OH)\textsubscript{2} electrodeposition method with different total charges. Figure 8e shows the J-V curves of perovskite PV cells with an electrodeposited NiO\textsubscript{x} layer deposited at various current densities. Figure 8f shows the J-V curves of the best-performing device (active area of 1.084 cm\textsuperscript{2}). Figure 8g shows the EQE spectra and integrated J\textsubscript{sc}. Reproduced with permission.\cite{81} Copyright 2017, WILEY-VCH.
The e-beam-deposited NiO thin film had larger grain size than the spin-cast film (Figure 8b,c), and the PSCs with the e-beam-deposited NiO showed higher efficiency and reproducibility (Figure 8d). Moreover, lower PL intensity of the perovskite film cast on the e-beam-deposited NiO confirmed its efficient charge extraction from the photoabsorber (Figure 8e).

Figure 7. a) Schematic representation of PLD. b) J-V curves (left) and EQE (right) for the best cell using nanostructured NiO film with thickness of 150 nm. c) Cross-sectional and top-view SEM images of the NiO films synthesized by PLD. d) Schematic images of thin, nanostructured, and disordered NiO films synthesized by PLD as an electron blocking layer/hole extraction layer in the perovskite-PCBM heterojunction PV cells. e) J-V curves of PSCs based on PLD-NiO films, deposited at various oxygen partial pressures. f) High-resolution XRD (HR-XRD) patterns of the NiO films synthesized by PLD. g) Transmittance spectra of the NiO films synthesized by PLD. Reproduced with permission. [82] Copyright 2015, WILEY-VCH.
It was also shown that more Ni$^{3+}$ in e-beam-evaporated NiO resulted in lower transmittance but it provided higher conductivity (Figure 8f). In addition, the solution-processed method has an uneven layer formation due to the accumulation of solution at the edge of the substrate, and thermal annealing treatment, generally required for the solution-processed NiO, is not desirable for large-scale production and is known to induce lots of defects in the thin film. Most of these disadvantages are expected to be resolved by the e-beam-evaporated NiO that can provide improved uniformity and compactness.

E-beam evaporation is one of the widely utilized methods for deposition of oxide-based thin films. The thickness and characteristics of the thin film can be easily adjusted through partial pressure or flow control of oxygen gas. However, there is still difficulty in commercialization because it requires high power and high-purity gas. To address these challenges, research has been conducted to form high-quality NiO thin films using e-beam deposition without the oxygen supply from outside.[84,85] This simplification is expected to make it a little closer to commercialization.

2.7. Sputtering Process

In this process, ionized gas particles having high energy are bombarded to the source target, from which atoms are ejected and condensed at the substrate. For the synthesis of NiO thin film, Ni target with O$_2$ gas or NiO$_x$ target can be utilized. As for the process with Ni target, Ni atoms are released from the target and react with oxygen atoms, consequently being deposited on the substrate in NiO$_x$ thin-film format. During this process, various factors such as the amount of oxygen, temperature of the substrate, and power affect the properties of NiO$_x$ thin film.[47,81,86,87] The growth orientation of sputtered NiO$_x$ films mainly depends on the sputtering power and the substrate temperature. Use of a new reactive magnetron sputtering technique was discussed for gaining good coverage and junctions between the perovskite and NiO$_x$ layer at low deposition temperature. The limitations of low FF and short-circuit current, commonly observed in sputtered NiO$_x$-derived PSCs, can be overcome through magnesium doping and low-oxygen partial pressure deposition. Li et al. demonstrated large-scale Mg-doped NiO$_x$ (over an area of 100 cm$^2$) using the sputtering process for PSC devices.[88] SEM images in Figure 9a,b show that morphology of perovskite is not significantly changed with Mg doping, but energy band of NiO can be improved for better alignment with the valence band edge of the perovskite layer (Figure 9c), inducing better charge extraction (Figure 9d). Consequently, the performances of PSC devices with the sputtered NiO$_x$ thin film, which were usually inferior to those with the solution-processed NiO$_x$ due to its low electrical conductivity and transmittance,[89–92] were enhanced with Mg doping, leading to 18.5% PCE by improving its optoelectronic properties.[88] The large-scale device also showed good uniformity and excellent stability in ambient condition (50–70% humidity), preserving 90% of its initial PCE after 600 h.

Sputtering process is suitable to fabricate high-quality thin films at low temperatures. Typically, radio frequency (RF)-type sputtering is used to deposit semiconductors such as NiO$_x$ that can be processed approximately ten times faster than DC sputtering methods. This method is also appropriate for doping various types of metals, which can control the electrical properties of

Figure 8. a) Schematic representation of e-beam deposition process. Reproduced with permission.[36] Copyright 2019, WILEY-VCH. Top-view SEM images of b) e-beam-deposited and c) spin-coated NiO$_x$ thin film on ITO glass. d) Histogram of perovskite PV cells with spin-coated and e-beam-deposited NiO$_x$ thin film. e) PL spectra of CH$_3$NH$_3$PbI$_3$ on spin-coated and e-beam-evaporated NiO$_x$ thin film and f) optical transmission spectra for ITO and NiO$_x$ deposited on ITO via spin coating and e-beam evaporation. Reproduced with permission.[83] Copyright 2018, American Chemical Society.
thin films. However, it is difficult to apply this approach to large-area PV devices because uneven layers are easily formed on the large-area substrates.

2.8. Atomic Layer Deposition (ALD)

A schematic representation of the atomic layer deposition (ALD) process is shown in Figure 10a. For NiO$_x$ thin-film formation by the ALD process, nickel-bis(1-dimethylamino-2-methyl-2-butanolate) and O$_3$ were utilized as precursors of Ni and O. The surface uniformity of NiO$_x$ film was confirmed by AFM (root mean square in the range from 0.3 to 0.4 nm) (Figure 10c), and the top-view SEM image of perovskite layer in Figure 10b ensured dense growth of crystallized grains with an average size of 100–150 nm.

The electrical conductivity and work function of the synthesized NiO$_x$ thin film decreased, as its thickness was increased to 7.5 nm, and they saturated over this thickness. Space-charge profiles depending on the physical film thickness of NiO$_x$ relative to Debye’s length ($L_D$) are shown in Figure 10e. If the thickness of NiO$_x$ is large enough compared with $L_D$, it behaves like an insulator, but if it is thin enough, $L_D$ starts to overlap, enhancing its work function and electrical conductivity. This is correlated with the results in Figure 10d, where the work function and electrical conductivity increase with the reduction in its thickness. Correspondingly, the maximum PCE at around 11.82% was obtained from the 5 nm NiO$_x$, because this thickness was sufficient for $L_D$ to be overlapped. The efficiency of PSCs could be further improved by post-heat treatment of NiO$_x$ film. Mott–Schottky plots in Figure 10g confirmed that work function and electrical conductivity of NiO$_x$ film increased with postannealing. X-ray photoelectron spectroscopy (XPS) analyses of pristine and annealed NiO$_x$ (Figure 10h) show that Ni oxidation states are changed and the amount of water and hydroxyl group is reduced after annealing, which improves the interfacial properties. Due to improvement in the work function and electrical conductivity, the PCE of annealed NiO$_x$-based PSCs was further enhanced to 16.4% (Figure 10i).

The ALD method has a great merit that can provide highly uniform thin films through direct chemical reactions on the surface of the substrate. However, this method demands not only high-purity precursors, but also multiple pulse–purge cycles, resulting in high cost and long processing time, compared with other methods. Therefore, to further improve the usability of this method, modification of the chemical reaction mechanism and reduction of the process time should be considered.

3. Modification of NiO$_x$ Properties and NiO$_x$/Perovskite Interface

Significant progress in NiO$_x$-based planar p–i–n PSCs is made, but their PCEs are still less than those of poly(triaryl amine) (PTAA)-based PSCs, showing the best efficiency of 23.0% in p–i–n structures, due to their low electrical conductivity, low transmittance, rough surface morphology, and unoptimized energy level. Doping NiO$_x$ thin films with extrinsic elements and modifying their surface with the organic and inorganic materials are widely investigated approaches to overcome those limitations as a HTM of PSC devices (Figure 11). Especially, dopants significantly influence their optoelectronic properties by adjusting their stoichiometry, oxidation states, and band structure; thus,
enhancement in conductivity, transmittance, and work function is observed. It is interesting to note that the stoichiometric NiO shows insulating behavior, but it exhibits p-type conductivity after the alteration of its stoichiometry by self-creating Ni vacancy.[95] Dopants also play a vital role in improving their crystallinity and alleviating surface traps, which contribute to improving the stability and reproducibility of PSC devices with negligible hysteresis loss. So far, various elements, such as transition metals, alkali metals, alkaline earth metals, nonmetal elements, and rare-earth metals, have been used as suitable dopants for NiO. Moreover, the surface functionalization of NiO films also has shown significant progress to improve the PCEs of PSCs.

### 3.1. Transition Metals Doping

The research works of transition metal doping in NiO are almost exclusively dominated by the p-type dopants like Co and Cu.[96,97] Nevertheless, some other elements such as Fe, Zn, Ag, and Al have also been attempted.[98–101] Chen et al. improved the carrier mobility of NiO by adding Cu, consequently increasing its conductivity significantly, verified by the conductive AFM (c-AFM) and I–V analysis (Figure 12a–c).[102] Theoretically calculated density of states (DOS) showed that Cu-doped NiO had the gap state at ≈0.7 eV above the Fermi level, whereas Ni vacancies in bulk NiO had the gap states at ≈1.3–2.0 eV above the Fermi level, which represented that Cu doping produced shallower acceptor levels, increasing hole concentration, conductivity, and work function. Furthermore, Cu⁺ could be substituted for Ni^{2+}, contributing to the improvement of carrier concentration and carrier mobility, and lower monomolecular Shockley–Read–Hall recombination decreased the recombination loss. Consequently, after adding Cu dopant, the inferior hole-extraction ability at the interface between NiO and perovskite was improved, enhancing the performances of PSC devices.

Bashir et al. also have intensively investigated Cu doping of NiO, and they observed an increment in electrical conductivity...
from $2 \times 10^{-3}$ to 0.20 S cm$^{-1}$ after the addition of 5% Cu dopant due to the reduction of bandgap from 3.25 eV (pristine NiO$_x$) to 3.12 eV, as shown in Figure 12d.$^{[103]}$ Moreover, Cu-doped NiO$_x$ had a higher crystallite size (19.6 nm) than pristine NiO$_x$ (12.89 nm), which indicated that the Cu content can promote the sustained growth of more widely dispersed nuclei of NiO$_x$ film. Thus, losses in $J_{sc}$ and FF in the pristine NiO$_x$-based PSCs were mitigated, and the PCE increased from 10.49 to 12.79%. Subsequently, Feng et al. studied the influence of Cu doping concentration on NiO$_x$ for PSCs.$^{[97]}$ The Cu doping did not change the surface morphology significantly, but it reduced the surface roughness (Figure 12e,f), which could be beneficial for the pinhole-free and smooth surface formation. Cu-doped NiO$_x$ HTL-based PSCs achieved the highest PCE of 20.41% with $J_{sc}$ of 23.17 mA cm$^{-2}$, as shown in Figure 12g.

Various research works have been conducted to further improve the functional properties of the Cu-doped NiO$_x$ HTL, such as UV-O$_3$ treatment,$^{[104]}$ organic surface modification,$^{[105]}$ addition of mesoporous layer, etc.$^{[106]}$ For instance, He et al. passivated Cu-doped NiO$_x$ HTLs using different small molecules such as glycine, cysteine, and mercaptoethylamine chloride. Among these, the PSC with cysteine-modified Cu:NiO$_x$ HTL exhibited the PCE over 18% mainly due to the improvement of $J_{sc}$ and $V_{oc}$.$^{[107]}$

In contrast, as a neighbor of Ni, Co was used as a suitable p-type dopant for NiO$_x$ due to the similar atomic radii of Co (152 pm) to that of Ni (149 pm). Huang et al. first introduced sputtered Co-doped NiO$_x$ HTL for planar PSCs. With the dramatic improvement in $J_{sc}$ and FF, they obtained 25% higher efficiency than that of undoped NiO$_x$ (from 9.46% to 12.61%).$^{[108]}$ The enhancement of hole mobility (from 3.718$^{2} \times 10^2$ to 3.232$^{2} \times 10^3$ cm$^2$V$^{-1}$S$^{-1}$) and improvement in surface roughness (from 12.691 to 5.545 nm) reduced the electrical and optical loss. As a result, the device showed only 90% PCE retention even after 10 days of storage without encapsulation. After that, Xie et al. fabricated planar PSCs using simple solution-processed Co-doped NiO$_x$ as HTL.$^{[109]}$ They investigated the effect of Co doping concentration on the optoelectronic properties of NiO$_x$. Based on optimization, 6 mol% of Co-doped NiO$_x$ exhibited a superior PCE of 18.2%, compared with 17.2% of undoped counterparts. All the device characteristics such as $J_{sc}$, $V_{oc}$, and FF increased by Co doping due to the enhanced electrical conductivity and reduced interfacial accumulation of charge.

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**Figure 11.** Schematic representation of different types of modifications used to modify the NiO$_x$ thin film and their impact on various properties.

**Figure 12.** a) c-AFM images of a) NiO$_x$ and b) Cu-doped NiO$_x$ thin films on ITO glass. c) $J$–$V$ curves of NiO$_x$ and Cu-doped NiO$_x$ measured using Au interdigitated electrodes with an electrode distance of 75 μm. Reproduced with permission.$^{[102]}$ Copyright 2018, WILEY-VCH. d) Comparison of energy bandgap pristine NiO$_x$ (3.25 eV) and Cu-doped NiO$_x$ (3.12 eV). Reproduced with permission.$^{[103]}$ Copyright 2019, Elsevier. e) Top-view SEM images of NiO$_x$ and Cu-doped NiO$_x$, thin film on FTO glass. f) AFM images of NiO$_x$ and Cu-doped NiO$_x$, thin film on FTO glass. g) $J$–$V$ curves of best performing PSC devices with Cu-doped NiO$_x$, deposited by PLD, and with undoped NiO$_x$. Reproduced with permission.$^{[107]}$ Copyright 2020, American Chemical Society.
carriers. Subsequently, Jung and coworkers improved the PCE of PSCs from 13.96% to 17.52% through 5% Co doping.\[110\] This improvement was mainly attributed to the enhanced electrical conductivity, better energy band alignment, and reduction of surface trap sites. The improved interface of Co–NiO/perovskite increased the grain size of perovskite to as high as 500 nm, which strongly reduced the trap sites at the grain boundary.

Silver (Ag) has been also used as a p-type dopant, and many research works have been conducted to improve the optoelectronic properties of metal oxide thin films using Ag as a dopant.\[111–113\] Wei et al. applied Ag dopant in NiO HTL by solution-based spin casting for p–i–n PSCs.\[89\] Their density functional theory (DFT) calculations showed that Ag occupied the substitutional Ni site (Ag_{Ni}), and 2 at% Ag was experimentally confirmed as an optimum condition. Compared with pristine NiO, the Ag-doped NiO increased the efficiency from 13.46% (pristine NiO) to 16.86% (2 at% Ag-doped NiO). This enhancement was strongly attributed to the appropriate Ag doping, which improved the functional properties of NiO films such as optical transparency, work function, electrical conductivity, and hole mobility. Furthermore, the efficient charge carrier extraction from the perovskite was also confirmed by PL lifetime decrease of the perovskite cast on Ag-doped NiO HTL from 17.0 to 5.5 ns. In addition, the PSCs with Ag-doped NiO stably operated without hysteresis and their stability was also improved.

Recently, aluminum (Al) doping strategy, which can increase the efficiency over 20%, was suggested.\[99\] The enhanced electrical conductivity of Al-doped NiO significantly reduced the nonradiative recombination losses at the interface between HTL and perovskite. From the Kelvin probe analysis, the surface potential of Al-doped NiO was confirmed to be 603 mV lower than that of the pristine one. The PSC device with Al-doped NiO HTL showed the PCE of 20.84% (J_{sc} of 23.43 mA cm\(^{-2}\), \(V_{oc}\) of 1.06 eV, and FF of 81.31%) with negligible hysteresis, which exceeded to the device with pristine NiO HTL (PCE 16.56%). Moreover, the devices with Al-doped NiO HTL retained 84.3% of their initial efficiency after 72 days and stabilized output PCE of 19.91% at maximum power point tracking.

In contrast, n-type element zinc (Zn) was also utilized as a dopant for NiO.\[109\] It is well known that zinc is an Earth-abundant low-cost element and it is more applicable for the solution-processed techniques. The 5% Zn-doped NiO exhibited high current flow with a scale of 5 mA in c-AFM measurement compared with that of NiO, which was attributed to the Zn dopant-induced charge carrier concentration. It also afforded high-quality perovskite with a large grain size of 500 nm, which reduced the trap site density at the grain boundaries. As a result, a noticeable improvement in PCE was observed from 10.43% to 13.72%.\[87\]

Chandrasekhar et al. tried iron (Fe) as a dopant for NiO HTL using NP ink at room temperature.\[105\] Fe doping resulted in a favorable work function and enhanced conductivity, which improved the hole extraction and reduced the recombination losses at the interface. The PCE of PSCs increased from 15.41% to 17.57% for rigid and from 13.37% to 14.42% for flexible devices with the Fe-doped NiO HTL. Table 1 and 2 show the performance of PSCs based on transition metals and alkali/alkaline element-doped NiO films.

The performances of PSCs have been significantly improved through various transition-metal-doped NiO\(_x\) compared with those with pristine NiO\(_x\). In terms of electrical properties, hole mobility and conductivity were increased, and the reduced roughness allowed the improvement of the morphology between NiO\(_x\) and perovskite layers. As an additional advantage, the energy barrier at the junction between NiO\(_x\) and perovskite can be reduced by fine tuning the work function of NiO\(_x\). Through these merits, it is expected that the transition metal doping technique of NiO\(_x\) could be applied to other oxide-based HTLs (i.e., CuO, SnO\(_2\), TiO\(_2\)).

### 3.2. Rare-Earth Metals Doping

Apart from the above-mentioned transition metals, rare-earth elements have been utilized as promising dopants for NiO HTLs. In general, rare-earth elements have been used to improve the magnetic and superconducting properties of metal oxide semiconductors.\[114\] However, their partially filled 4f orbitals and vacant 5d orbitals exhibited better energy-level structures of NiO.\[115\] Furthermore, its large transmission coefficient and higher optical bandgap improved the optical transparency of NiO\(_x\) without compromising its conductivity. The ionic radius of the rare-earth ion is greater than that of Ni\(_{2+}\) which induces more interstitial or substitutional sites. It exhibits donor-like behavior with the association of oxygen vacancies.\[116\] Chen et al. improved the conductivity of the NiO\(_x\) HTL using various trivalent rare-earth ions such as Ce, Nd, Eu, Tb, and Yb as dopants.\[117\] The results demonstrated that 3% europium (Eu) doping produced a smooth and compact NiO\(_x\) thin film even with high conductivity, and it was advantageous to grow the perovskite layer having larger grain size. Consequently, the carrier extraction property was enhanced and recombination was suppressed. The PCE of device was enhanced from 12.20% to 15.06%, which was a 23.4% increase. Subsequently, Goumri–Said et al. found that Eu doping on NiO\(_x\) would improve the transmittance and optical bandgap of NiO\(_x\) film within a certain doping limit. The Urbach energy level increased with the increase in Eu dopings.\[118\] Hu et al. studied the effect of yttrium (Y) doping on the NiO\(_x\) HTL for p–i–n PSCs. They added different concentrations (0–10%) of Y dopant to amorphous NiO\(_x\), and their XPS results confirmed that the trivalent Y\(^{3+}\) was in NiO\(_x\). The PSCs, built on 5% Y-doped NiO\(_x\) HTL, exhibited the superior PCE of 16.31% (\(J_{sc}\) of 23.82 mA, \(V_{oc}\) of 1.0 V, and FF of 68%), which was 27.62% enhancement compared with that of PSCs on undoped NiO\(_x\) HTL.\[119\] Teo et al. incorporated lanthanum (La) into NiO\(_x\) for defect passivation purposes.\[120\] The PL quenching and the decrement in charge transfer resistance (\(R_{ct}\)) (from 3100 \(\Omega\) to 1200 \(\Omega\)) confirmed that La effectively passivated the trap states in pristine NiO\(_x\). In addition, La altered the VBM level of NiO\(_x\) consequently enhancing its hole transportation property. Moreover, La doping drastically improved the stability of the devices, and 95% efficiency was retained even after 50 days. Table 3 shows the performance of PSCs based on rare-earth element-doped NiO\(_x\) films.

The rare-earth metal doping method allowed the formation of dense and compact NiO\(_x\) thin films even with improved properties. The improved quality of NiO\(_x\) thin films increased the
crystallinity and grain size of perovskite layer, resulting in enhanced PV parameters. Although this doping approach is not very suitable for commercialization due to the use of rare and expensive metals, it can be evaluated to broaden the insight into NiO_x doping mechanisms using various metal elements.

### 3.3. Multielements Codoping Strategy

The former section is about strategies, utilizing single element for NiO_x doping to improve its surface morphology, conductivity, and band alignment. However, this approach often reduces the transmittance of the thin film,[121,122] degrading the performances of p–i–n-structured PSCs.[123] This can be improved by reducing the thickness of the film.[108] However, the preparation of such an ultrathin film without defects like pinholes requires considerable expertise. Alternatively, the multicomponent doping approach has been extensively investigated as an efficient way to improve its transmittance, and various codoping strategies were developed to enhance the performance of PSCs. Chen et al. demonstrated that Li and Mg codoping improved lattice stability due to the small difference in the ionic radii of Li (0.76 Å), Mg (0.71 Å), and Ni (0.69 Å).[124] Figure 13a shows the schematic representation of Li- and Mg-codoped NiO_x-based PSC devices. Li and Mg codoping also enhanced the

### Table 1. Summary of the device performances of transition metal-doped NiO_x thin film-based PSCs

| Doping  | Method                  | Device configuration                                                                 | Area [cm²] | Voc [V] | Jsc [mA cm⁻²] | FF  | Initial PCE [%] | Retained PCE [%] | Storage condition                                                                 | Storage Time [days] | Year | Ref. |
|---------|-------------------------|-------------------------------------------------------------------------------------|-----------|---------|---------------|-----|----------------|------------------|-----------------------------------------------------------------|---------------------|------|------|
| Cu      | PLD                     | FTO/NiO_x/FAx₂MA₇₋₈Pb₃X₂/Csb₁₋ₓ/PCBM/RhB/LiF/Ag                                  | 0.11      | 1.11   | 23.17        | 79.1| 20.19         | 93.9             | 20% relative humidity (RH)/25°C (w/o encapsulation)             | 30                  | 2020 | [97] |
| Co      | Spin coating            | FTO/NiO_x/CH₃NH₃PbI₃/PCBM/PEI/Ag                                                   | 0.05      | 1.09   | 20.46        | 79.8| 17.77         | 80.0             | N₂-filled glove box (w/o encapsulation)                           | 10.42               | 2020 | [96] |
| Al      | Spin coating            | ITO/NiO_x/CH₃NH₃PbI₃/PCBM/Am-TiO₂/Ag                                               | 0.40      | 1.06   | 24.34        | 81.3| 20.84         | 84.3             | Glove box (w/o encapsulation)                                    | 72                  | 2020 | [99] |
| Cu      | Spin coating            | ITO/NiOₓ/(CH₃NH₃PbI₃)_2/PCBM/Ag                                                     | 0.05      | 1.03   | 21.24        | 72.5| 15.88         | N/A              | N/A                                                            | N/A                 | 2020 | [170]|
| Fe      | Spin coating            | FTO/NiO_x/CH₃NH₃PbI₃/PCBM/Ag                                                       | 0.04      | 1.0    | 19.21        | 84.5| 17.61         | N/A              | N/A                                                            | N/A                 | 2019 | [101]|
| Co      | Spin coating            | ITO/NiO_x/CH₃NH₃PbI₃/PCBM/bs-Cos/Ag                                                | 0.01      | 1.04   | 22.97        | 74.0| 17.52         | 94.0             | N/A                                                            | 30                  | 2019 | [110]|
| Y       | Sol.–gel                | FTO/NiO_x/CH₃NH₃PbI₃/PCBM/Au                                                        | 0.08      | 1.00   | 23.82        | 68.0| 16.31         | N/A              | N/A                                                            | N/A                 | 2018 | [119]|
| Zn      | Spin coating            | ITO/NiO_x/CH₃NH₃PbI₃/PCBM/bs-Cos/Ag                                                | 0.11      | 1.03   | 21.84        | 61.0| 13.72         | N/A              | N/A                                                            | N/A                 | 2018 | [100]|
| Ag      | Spin coating            | ITO/NiOₓ/(CH₃NH₃PbI₃)_2/PCBM/Ag                                                     | 0.40      | 1.07   | 19.42        | 79.0| 16.42         | 80.0             | 30 ± 2% RH (w/o encapsulation)                                   | 30                  | 2018 | [98] |
| Co      | Spin coating            | ITO/NiO_x/CH₃NH₃PbI₃/PCBM/PEI/Ag                                                   | 0.04      | 1.05   | 22.3         | 79.0| 18.60         | N/A              | N/A                                                            | N/A                 | 2018 | [109]|
| Zn      | Sol.–gel                | FTO/NiO_x/CH₃NH₃PbI₃/PCBM/PCBM/Ag                                                  | 0.03      | 1.10   | 22.8         | 78.0| 19.60         | 90.0             | Dry air                                                        | 30                  | 2018 | [171]|
| Cu      | Spin coating            | FTO/NiO_x/CH₃NH₃PbI₃/PCBM/Ag                                                       | 0.03      | 1.06   | 20.79        | 64.0| 14.88         | 90.0             | 60% RH/30°C (w/o encapsulation)                                  | 10                  | 2018 | [172]|
| Cu      | Spin coating            | ITO/NiO_x/CH₃NH₃PbI₃/Csb₁₋ₓ/PCBM/Ag                                                | 0.08      | 1.12   | 22.28        | 81.2| 20.26         | 95.0             | 50–60% RH/23°C (with encapsulation)                              | 41.7                 | 2018 | [102]|
| Cu      | Sol.–gel                | FTO/NiO_x/mp-NiO_x/CH₃NH₃PbI₃/PCBM/Ag                                              | 0.06      | 1.11   | 21.58        | 82.0| 19.62         | 94.0             | 30% RH/25°C (w/o encapsulation)                                  | 41.7                 | 2018 | [173]|
| Cu      | Combustion              | ITO/NiO_x/Cysteine/CH₃NH₃PbI₃/PCBM/Bphen/Al                                         | 0.12      | 1.11   | 23.60        | 76.0| 18.30         | 48.0             | 60% RH/25°C (w/o encapsulation)                                  | 5                   | 2017 | [107]|
| Cu      | Spin coating            | ITO/NiO_x/CH₃NH₃PbI₃/PCBM/BCP/Ag                                                   | 0.10      | 1.11   | 20.76        | 81.0| 18.66         | 86.0             | Ambient atmosphere/25°C (w/o encapsulation)                      | 30                  | 2017 | [174]|
| Cu      | Spin coating            | ITO/NiO_x/CH₃NH₃PbI₃/PCBM/Ag                                                       | N/A       | 1.12   | 23.07        | 77.1| 20.14         | N/A              | N/A                                                            | N/A                 | 2017 | [175]|
| Cu      | Spin coating            | ITO/NiO_x/CH₃NH₃PbI₃/PCBM/LiF/Al                                                    | N/A       | 1.04   | 18.10        | 75.5| 14.20         | N/A              | N/A                                                            | N/A                 | 2017 | [176]|
| Cu      | Sol.–gel                | ITO/NiO_x/CH₃NH₃PbI₃/PCBM/Ag                                                       | N/A       | 1.02   | 17.10        | 71.0| 12.20         | N/A              | N/A                                                            | N/A                 | 2016 | [104]|
| Co      | Magnetron sputtering    | FTO/NiO_x/CH₃NH₃PbI₃/PCBM/Ag                                                       | 0.07      | 1.01   | 20.02        | 63.4| 12.63         | 90.0             | 60% RH/30°C (w/o encapsulation)                                  | 10                  | 2012 | [108]|
| Cu      | Combustion              | ITO/NiO_x/CH₃NH₃PbI₃/Csb₁₋ₓ/Ag                                                     | 0.03      | 1.05   | 22.23        | 76.0| 17.74         | N/A              | N/A                                                            | N/A                 | 2015 | [78]  |
| Cu      | Sol.–gel                | ITO/NiO_x/CH₃NH₃PbI₃/PCBM/bs-Cos/Ag                                                | 0.03      | 1.11   | 19.01        | 73.0| 15.40         | 90.0             | Ambient air (w/o encapsulation)                                  | 10                  | 2014 | [177]|

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Li- and Ag-codoped NiO (Li$_x$C$_{10-x}$/Ni$_x$Ag$_{1-x}$) environment and found that MAPbI$_3$, cast on pristine NiO$_x$, Li-doped NiO$_x$, and Ag-doped NiO$_x$ thin films, as shown in Figure 13b. The crystal structures of pristine NiO$_x$ and Li- and Ag-codoped NiO$_x$ along with their DOS are shown in Figure 13c. The theoretically calculated DOS showed that Li- and Ag-codoped NiO$_x$ had shallower acceptor levels than those of the pristine NiO$_x$, beneficial to the enhancement of hole concentration. The best efficiency of Li- and Ag-codoped NiO$_x$ PSCs was 19.24% with 30 days of stability (95% retained) under 30% humidity condition.

Niu et al. investigated the effect of oxygen vacancy by annealing the LiMgNiO$_x$ film in dry air and N$_2$ environment and found 10% enhancement of hole concentration. The best efficiency was 19.24% with 30 days of stability (95% retained) under 30% humidity condition.

Table 2. Summary of the device performances of alkali metal-doped NiO$_x$ thin film-based PSCs, alkali metal elements, synthesis method of NiO$_x$, device configuration, cell area, open-circuit voltage, short-circuit current, FF, initial PCE, retained PCE, storage condition, storage time, and year of publication.

| Dopant | Method | Device configuration | Area [cm$^2$] | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] | FF [%] | Initial PCE [%] | Retained PCE [%] | Storage Condition | Storage time (days) | Year | Ref. |
|--------|--------|----------------------|--------------|-------------|----------------|--------|----------------|----------------|------------------|--------------------|------|------|
| Li     | Spin coating | ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PCBM/Ag | 0.13 | 1.01 | 18.30 | 68.0 | 12.60 | N/A | N/A | 2019 | [178] |
| K      | Spin coating | FTO/NiO$_x}$/C$_{2}$(FA$_3$)PbI$_3$/Ag (with encapsulation) | 0.04 | 1.13 | 20.53 | 74.0 | 17.02 | 80.0 | N/A | 2019 | [179] |
| Rb     | Sol–gel | ITO/NiO$_x$/C$_{2}$(FA$_3$)PbI$_3$/Br$_x$/PCBM/TiPO/Ag | 0.31 | 1.05 | 21.77 | 75.3 | 17.21 | N/A | N/A | 2019 | [180] |
| Ba     | Spin coating | FTO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PCBM/BCP/Ag | 0.06 | 1.10 | 22.24 | 73.7 | 17.94 | N/A | N/A | 2019 | [181] |
| Sr     | Spin coating | FTO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PCBM/Ag | 0.06 | 1.14 | 27.56 | 76.6 | 19.49 | 90.0 | 15% RH/25 °C (w/o encapsulation) | 30 | 2019 | [181] |
| Mg     | Spin coating | FTO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PCBM/BCP/Ag | 0.06 | 1.10 | 22.44 | 74.4 | 18.29 | N/A | N/A | 2019 | [181] |
| Ca     | Spin coating | FTO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PCBM/Ag | 0.06 | 1.13 | 23.20 | 74.8 | 18.75 | N/A | N/A | 2019 | [181] |
| Sr     | Spin coating | FTO/NiO$_x$/[FA$_3$]$x$(MA$_{0.15}$)$_{0.85}$PbI$_3$/PCBM/Ag | 0.04 | 1.14 | 27.56 | 76.6 | 19.49 | 90.0 | 15% RH/25 °C (w/o encapsulation) | 30 | 2019 | [181] |
| Li     | Sol–gel | ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PCBM/Ag | N/A | 1.00 | 20.89 | 74.0 | 15.41 | N/A | N/A | 2018 | [182] |
| Mg     | Sputtering | ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PCBM/Ag | 0.10 | 1.08 | 21.30 | 79.0 | 18.20 | 90.0 | 50–70% RH/25 °C (with encapsulation) | 25 | 2017 | [88] |
| Li     | Spin coating | ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/Cl$_{0.3}$/PCBM/Al | 0.05 | 1.12 | 21.79 | 73.6 | 17.96 | N/A | N/A | 2017 | [132] |
| Cs     | Spin coating | FTO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PCBM/Ag | 0.01 | 1.12 | 21.77 | 79.3 | 19.35 | 98.0 | Ar-filled glove box (w/o encapsulation) | 70 | 2017 | [185] |
| Li     | PLD | ITO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/Cl$_{0.3}$/PCBM/Ag | 0.07 | 1.05 | 22.80 | 64.2 | 15.51 | 86.5 | Glove box (≥28 °C) (w/o encapsulation) | 20 | 2017 | [102] |
| Cs     | Sol–gel | FTO/NiO$_x$/C$_{2}$(FA$_3$)PbI$_3$/MAPbI$_3$/PCBM/BCP/Ag | 0.16 | 1.03 | 21.4 | 78.0 | 17.20 | N/A | N/A | 2018 | [186] |

Table 3. Summary of the device performance of rare-earth metal-doped NiO$_x$ thin film-based PSCs, rare earth metal elements, synthesis method of NiO$_x$, device configuration, cell area, open-circuit voltage, short-circuit current, FF, initial PCE, retained PCE, storage condition, storage time, and year of publication.

| Dopant | Method | Device configuration | Area [cm$^2$] | $V_{oc}$ [V] | $J_{sc}$ [mA cm$^{-2}$] | FF [%] | Initial PCE [%] | Retained PCE [%] | Storage condition | Storage time (days) | Year | Ref. |
|--------|--------|----------------------|--------------|-------------|----------------|--------|----------------|----------------|------------------|--------------------|------|------|
| Ce     | Spin coating | FTO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PCBM/Ag | 0.10 | 1.03 | 21.60 | 58.6 | 12.97 | N/A | N/A | 2019 | [117] |
| Nd     | Spin coating | FTO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PCBM/Ag | 0.10 | 0.94 | 19.37 | 70.6 | 12.86 | N/A | N/A | 2019 | [117] |
| Eu     | Spin coating | FTO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PCBM/Ag | 0.10 | 1.03 | 21.96 | 66.6 | 15.06 | 97.0 | 25–55% RH/25–35 °C (with encapsulation) | 10 | 2017 | [117] |
| Yb     | Spin coating | FTO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PCBM/Ag | 0.10 | 0.99 | 21.58 | 64.1 | 13.70 | N/A | N/A | 2019 | [117] |
| Tb     | Spin coating | FTO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PCBM/Ag | 0.10 | 0.98 | 20.08 | 69.0 | 13.58 | N/A | N/A | 2019 | [117] |
| La     | Spin coating | FTO/NiO$_x$/CH$_3$NH$_3$PbI$_3$/PCBM/Ag | 0.08 | 1.02 | 20.25 | 73.0 | 15.03 | 95.0 | Moisture-free desiccator (w/o encapsulation) | 30 | 2018 | [120] |
that the sample, prepared in dry air, had small energy difference between the VBM values of HTM and perovskite, beneficial to charge transfer. The average lifetime of the sample, prepared in dry air, was 2.2 ns, shorter than that of the sample, prepared in nitrogen atmosphere (3.1 ns), as shown in Figure 13e, and this led to the efficient charge transfer between LiMgNiO$_x$ and perovskite layer. The device fabricated on dry air-annealed LiMgNiO$_x$ layer showed 19.2% efficiency with negligible hysteresis.
Another codoping approach with Li and Cu was reported by Wu and coworkers. They found that the optimum doping concentrations of Li and Cu were 2% and 3%, respectively. The hole mobility of 2% Li and 3% Cu-doped NiOx film was shown to be 165.9 cm²/V·s, much higher than that of 5% Cu single-element-doped NiOx film (100.9 cm²/V·s). The improvement in hole mobility enhanced the electrical conductivity, which led to the increment in the charge extraction capability of NiOx film. PL quenching behaviors of perovskites cast on various HTMs in Figure 13f confirm the efficient charge extraction at the interface between the 2% Li- and 3% Cu-doped NiOx and perovskite. The transmittance of 2% Li- and 3% Cu-doped NiOx layer was also enhanced compared with that of 5% Cu-doped NiOx (Figure 13g). Consequently, the 2% Li- and 3% Cu-doped NiOx thin-film-based PSC showed 14.53% PCE, which was around 25% higher than that of the pure Cu-doped NiOx-based PSC.

Wang et al. reported Li and Co doping strategy, which could improve the properties of NiOx thin films. The efficiency of PSCs fabricated on Li0.10Co0.05NiO0.85O thin films, 20.1%, superior to that of PSCs, prepared on any other codoped NiOx thin films, was reported. Recently, Li and Pb codoping strategy was also studied, and the PSC device with 17.02% efficiency, higher than that of PSCs on an undoped layer (15.4%), was reported. Table 4 shows the performance of PSCs based on codoped element-added NiOx films.

In addition to the monometal doping methods, multi-metal element codoping methods have also been actively studied. Even if this method is slightly more complex, it has shown that the electrical and optical properties of the NiOx thin films can be effectively controlled by changing the composition of each metal element. By adjusting the composition of metal elements, the oxygen vacancy state, which can tune the work function of NiOx, can be changed efficiently. Therefore, designing multielements doping strategy can be considered as a creative approach to improve the performances of PSCs.

### 3.4. Surface Modification of NiOx

Surface modification is one of the widely utilized methods to modify the surface properties, electrical conductivity, morphology, and work function. As for NiOx film, Ni²⁺ of the Ni atom vacancy is replaced by Ni³⁺, which creates the shallow acceptor level. This observation helps to understand the requirement of substitutional doping and thus the modification of the oxidation states of NiOx film.

Surface contamination often reduces the work function of NiOx thin film. UV–O₃ and O₂ plasma treatment have been widely utilized to remove those, but the property of the films is also modified with these processes. For instance, the work function at around 5.24–5.4 eV was reported after the UV–O₃ treatment, which was lower than that of the commonly reported value (4.8 eV). Moreover, these are not absolute values and strongly depend on the synthetic methods of NiOx and perovskite thin films. Different from those, functionalization of NiOx thin films with organic and hybrid materials has been investigated as an efficient, reproducible, and less synthesis-sensitive approach to improve the performances of the PSCs.

Organic molecules can be utilized to modify NiOx thin film. It has been reported that 6T-CNQ extracted electrons from NiOx due to its high electron affinity and used a strong connection with the surface of HTM. This ensures the stable growth of perovskite thin film on the organic molecule-doped NiOx. Energy-level diagrams of NiOx organic layer, and perovskite are shown in Figure 14a. The energy-level differences between VBM and Fermi energy level significantly reduced from 0.58 to 0.29 eV after 6T-CNQ doping (Figure 14b). The work functions (VBM levels) of pristine and 6T-CNQ-included NiOx film are 4.63 (5.21) and 5.07 (5.36) eV, respectively, as shown in Figure 14c–e, confirming the fast electron transfer from NiOx to 6T-CNQ. The cross-sectional SEM image of the device, along with element mapping, is shown in Figure 14f. The maximum device efficiency, based on 6T-CNQ-doped NiOx thin film, was 20.86% (Figure 14g) without hysteresis (Figure 14h, i).

### Table 4. Summary of the device performance of co-doped NiOx thin film-based PSCs, co-doped elements, synthesis method of NiOx, device configuration, cell area, open-circuit voltage, short-circuit current, FF, initial PCE, retained PCE, storage condition, storage time, and year of publication.

| Dopant | Method | Device configuration | Area [cm²] | Voc [V] | Jsc [mA·cm⁻²] | FF [%] | Initial PCE [%] | Retained PCE [%] | Storage condition | Storage time [days] | Year | Ref. |
|--------|--------|----------------------|------------|--------|-------------|------|---------------|----------------|-----------------|-----------------|------|-----|
| Li & Mg | Spray pyrolysis | FTO/NiOₓ/CH₃NH₃PbI₃/PCBM/Ti(Nb)Oₓ/Ag | 1.02 | 1.07 | 20.60 | 74.8 | 16.20 | 97.0 | Dry cabinet < 20% RH (w/o encapsulation) | 41.7 | 2015 | [124] |
| Li & Mg | Spray pyrolysis | FTO/NiOₓ/FA₀.₃₃MA₀.₆₇PbI₃(0.85Br₀.₁₅)/PCBM/Ag | 1.02 | 1.08 | 21.95 | 78.4 | 18.21 | 90.0 | 25% RH/25 °C (with encapsulation) | 41.7 | 2016 | [187] |
| Li & Cu | Spin coating | FTO/NiOₓ/CH₃NH₃PbI₃/PCBM/Ag | N/A | 0.97 | 20.28 | 71.8 | 14.04 | N/A | N/A | N/A | 2016 | [127] |
| Li & Mg | Spin coating | FTO/NiOₓ/CsFAMAPbI₃/PCBM/Ag | 0.16 | 1.08 | 22.55 | 79.0 | 19.20 | ≈100.0 | 55% RH/25 °C (w/o encapsulation) | 15 | 2018 | [126] |
| Li & Ag | Spin coating | FTO/NiOₓ/CH₃NH₃PbI₃/PCBM/BCP/Ag | N/A | 1.13 | 21.29 | 80.0 | 19.24 | 0.95 | 30 ± 2% RH/25 °C (w/o encapsulation) | 30 | 2018 | [125] |
| Li & Co | Spin coating | FTO/NiOₓ/MAFAPbI₃/PCBM/BCP/Ag | 0.07 | 1.09 | 23.80 | 78.0 | 20.10 | 0.94 | 30–40% RH/25 °C (w/o encapsulation) | 30 | 2019 | [128] |
| Li & Pb | Spin coating | FTO/NiOₓ/CH₃NH₃PbI₃/PCBM/BCP/Ag | N/A | 1.01 | 21.31 | 78.8 | 17.02 | N/A | N/A | N/A | 2020 | [129] |
Approaches to graft self-assembled monolayers on NiO\(_x\) surface by forming bonds through amines, carboxylates, and thiols with phosphonic acid have been introduced. The functionalization of NiO\(_x\) with the organic monolayer improved surface chemistry, and it was beneficial to grow defect-free absorber layer. It was also advantageous to stabilize the interface between NiO\(_x\) and perovskite and control their work functions for improving the performances of PSCs. Zhang et al. modified the NiO\(_x\) film with polymeric PTAA, and this could reduce the charge recombination at the interface between perovskite and PTAA/NiO\(_x\) due to gradient band alignment. The calculated trap densities on NiO\(_x\) and PTAA/NiO\(_x\) films were 1.06 \(\times\) 10\(^{16}\) and 6.58 \(\times\) 10\(^{15}\) cm\(^{-3}\), respectively, and the perovskite layer on PTAA/NiO\(_x\) film had better quality with larger grain size. A similar effect was reported by the alkali halides such as NaCl and KCl.

Diethanolamine (DEA) monolayer was also utilized to modify NiO\(_x\), which improved the surface morphology of the perovskite layer, but it does not affect the work function, and thus \(V_{oc}\) of PSCs remained almost the same. He et al. used cysteine and mercaptopethalmine (Merc) to modify the CuNiO\(_x\) surface. Carboxyl group or amine chlorate interacted with CuNiO\(_x\), and the sulfhydryl group worked as the anchoring group, which formed the Ni—S bond. The remaining \(-\text{NH}_3\) groups were exposed for the interaction with perovskite materials. Additional carboxyl groups helped to improve the work function.

Figure 14. a) Energy band alignment of solar cell along with the chemical structure of F6TCNNQ. b) Valance band spectra of NiO\(_x\) and NiO\(_x\)/F6TCNNQ thin film. c) UPS spectrum of NiO\(_x\) and NiO\(_x\)/F6TCNNQ thin film. d) Band bending of NiO\(_x\) thin film-based solar cell. e) Band bending of NiO\(_x\)/F6TCNNQ thin film-based solar cell. f) SEM image and elemental mapping of NiO\(_x\)/F6TCNNQ thin film-based solar cell. g) Comparison of PCE of NiO\(_x\) and NiO\(_x\)/F6TCNNQ thin film-based solar cell. h) Hysteresis curve of NiO\(_x\) thin film-based solar cell and i) hysteresis curve of NiO\(_x\)/F6TCNNQ thin film-based solar cell. Reproduced with permission. Copyright 2018, WILEY-VCH.
of the HTL. The performances of the devices were improved to 18.3% due to the highly crystallized film and favorable interfacial contact, enhancing their $J_{SC}$ and $V_{OC}$. Tavakoli and coworkers used poly $(9,9$-bis $(3$'-(N,N-dimethyl-N-ethylammonium)-propyl)-2,7-fluorene-alt-2,7-(9,9-diocetylfluorene)) dibromide (PFN-P2) to modify the NiO$_x$ film.\textsuperscript{[139]} By introducing PFN-P2 to NiO$_x$, surface roughness reduced from 13 to 6 nm, which reduced recombination and enhanced charge transfer at the interface between NiO$_x$ and perovskite. About 20.5% efficiency was achieved after modifying the NiO$_x$ thin film with PFN-P2.

We newly synthesized a series of triphenylamine-imidazole (TPI) derivatives having different numbers of methoxy units from 2 to 6 (TPI-2MEO, TPI-4MEO, and TPI-6MEO) for passivating unsaturated bonds of NiO$_x$ and defects in perovskite, simultaneously.\textsuperscript{[140]} The chemical structures of the TPIs with different numbers of methoxy unit are shown in Figure 15a. IR spectrum of TPI-6MEO/NiO$_x$ showed an additional Ni–N vibrational peak at around 526 cm$^{-1}$, which was not observed from the pristine NiO$_x$. This confirmed that N atoms of organic molecules formed covalent bonds with Ni atoms of NiO$_x$ layer, saturating oxygen vacancy. Moreover, Pb–O stretching peaks in Raman spectrum of TPI-6MEO/perovskite also represented the passivation of Pb$^{2+}$ defects in perovskite by methoxy units in TPIs. In addition, the HOMO levels of molecules were deepened to have better alignment with the VBM of perovskite as the number of methoxy units increased (Figure 15b). The cross-sectional SEM image of the device and top-view SEM image of perovskite are shown in Figure 15c,f, respectively. After passivating defects in both NiO$_x$ and perovskite with organic functional groups, steady-state (Figure 15g) and time-resolved PL (Figure 15i) of perovskite were efficiently quenched, and the absorbance of perovskite was enhanced. Consequently, the device performance was improved with TPI-6MEO, which reached 18.42% (Figure 15c). The PSC devices did not show hysteretic behavior (Figure 15d) and represented superior stability (Figure 15j). Table 5 shows the performances of PSCs, fabricated on the surface-functionalized NiO$_x$ thin films.

The solution-based processes are generally utilized to form NiO$_x$ thin films due to their simplicity and cost-effectiveness. However, the NiO$_x$ thin films formed by these methods often

Figure 15. a) Chemical structure of methoxy-functionalized TPI. b) Energy band alignment of different layers of solar cells. c) $J$–$V$ curve of pristine and methoxy-functionalized TPI NiO$_x$ thin film. d) Hysteresis curve of pure NiO$_x$ and NiO$_x$/TPI-6MEO-based solar cell. e) SEM image of different layers of solar cells. f) Surface morphology of perovskite layer. g) PL spectrum of NiO$_x$ and NiO$_x$/TPI-6MEO thin film. h) Absorption spectrum of NiO$_x$ and NiO$_x$/TPI-6MEO thin film. i) Carrier lifetime of pristine and methoxy-functionalized TPI NiO$_x$ thin film and j) comparison of stability of NiO$_x$ and NiO$_x$/TPI-6MEO thin film-based solar cell. Reproduced under the terms of a CC-BY license.\textsuperscript{[140]} The Authors, published by Copyright 2019, WILEY-VCH.
Table 5. Summary of the device performance of surface functionalized NiOx thin film-based PSCs, surface functionalized materials, synthesis method of NiOx, device configuration, cell area, open-circuit voltage, short-circuit current, FF, initial PCE, retained PCE, storage condition, storage time and year of publication.

| Dopant         | Method       | Device configuration                                  | Area [cm²] | Voc [V] | Jsc [mA cm⁻²] | FF   | Initial PCE [%] | Retained PCE [%] | Storage condition | Storage time [days] | Year Ref. | Ref. |
|----------------|--------------|-------------------------------------------------------|------------|---------|----------------|------|-----------------|------------------|-------------------|---------------------|-----------|-----|
| UV             | Spin coating | ITO/NiOx(CH₃NH₃PbI₃)/PCBM/Al                          | N/A        | 0.07    | 2.05          | 15.40| 47.0 7.6        | N/A              | N/A               | N/A                 | 2014  [61] |     |
| UV – O₂        | Spin coating | ITO/NiOx(CH₃NH₃PbI₃)/PCBM/BCP/Al                      | N/A        | 0.06    | 0.92          | 12.43| 68.0 7.8        | N/A              | N/A               | N/A                 | 2014  [62] |     |
| PVP/UV – O₂    | Spin coating | ITO/ P-UV-O₂NiOx(CH₃NH₃PbI₃)/PCBM/BCP/Al             | N/A        | 1.08    | 0.94          | 16.0 | 3.8 6.7         | N/A              | N/A               | N/A                 | 2014  [63] |     |
| DEA            | Spin coating | ITO/NiOx/DEA(CH₃NH₃PbI₃)/PCBM/BCP/Al                 | N/A        | 0.13    | 0.11          | 10.0 | 3.0 14.1        | N/A              | N/A               | N/A                 | 2014  [64] |     |
| SAMs           | Spin coating | ITO/NiOx(SAM)/CH₃NH₃PbI₃/PCBM/BCP/Al                 | N/A        | 0.12    | 0.01          | 1.85 | 1.9 1.0         | N/A              | N/A               | N/A                 | 2014  [65] |     |
| DEA            | Spin coating | ITO/NiOx/DEA(CH₃NH₃PbI₃)/PCBM/BCP/Al                 | N/A        | 0.14    | 0.11          | 11.0 | 3.0 12.1        | N/A              | N/A               | N/A                 | 2014  [66] |     |
| cysteine       | Spin coating | ITO/CuNiOx(CH₃NH₃PbI₃)/PCBM/BCP/Al                    | N/A        | 0.11    | 1.75          | 12.9 | 2.0 20.1        | N/A              | N/A               | N/A                 | 2014  [67] |     |
| Merc           | Spin coating | ITO/CuNiOx(CH₃NH₃PbI₃)/PCBM/BCP/Al                    | N/A        | 0.17    | 1.75          | 12.9 | 2.0 20.1        | N/A              | N/A               | N/A                 | 2014  [68] |     |
| PhNa-1T        | Spin coating | ITO/CuNiOx(CH₃NH₃PbI₃)/PCBM/BCP/Al                    | N/A        | 0.12    | 0.01          | 1.85 | 1.9 1.0         | N/A              | N/A               | N/A                 | 2014  [69] |     |
| PTAA           | Spin coating | ITO/CuNiOx(CH₃NH₃PbI₃)/PCBM/BCP/Al                    | N/A        | 0.14    | 0.11          | 11.0 | 3.0 12.1        | N/A              | N/A               | N/A                 | 2014  [70] |     |
| FDA            | Spin coating | ITO/CuNiOx(CH₃NH₃PbI₃)/PCBM/BCP/Al                    | N/A        | 0.14    | 0.11          | 11.0 | 3.0 12.1        | N/A              | N/A               | N/A                 | 2014  [71] |     |
| F6TCNNQ        | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.13    | 1.95          | 2.0 20.1        | N/A | 0.95          | N/A              | N/A               | N/A                 | 2014  [72] |     |
| PFN-P2         | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.13    | 1.95          | 2.0 20.1        | N/A | 0.95          | N/A              | N/A               | N/A                 | 2014  [73] |     |
| UV – O₂        | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.12    | 0.01          | 1.85 | 1.9 1.0         | N/A              | N/A               | N/A                 | 2014  [74] |     |
| Na₂NaCl        | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.14    | 0.11          | 11.0 | 3.0 12.1        | N/A              | N/A               | N/A                 | 2014  [75] |     |
| KCl            | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.13    | 1.95          | 2.0 20.1        | N/A | 0.95          | N/A              | N/A               | N/A                 | 2014  [76] |     |
| TPI            | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.12    | 0.01          | 1.85 | 1.9 1.0         | N/A              | N/A               | N/A                 | 2014  [77] |     |
| TPI-2MeO       | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.13    | 1.95          | 2.0 20.1        | N/A | 0.95          | N/A              | N/A               | N/A                 | 2014  [78] |     |
| TPI-4MeO       | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.14    | 0.11          | 11.0 | 3.0 12.1        | N/A              | N/A               | N/A                 | 2014  [79] |     |
| TPI-6MeO       | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.13    | 1.95          | 2.0 20.1        | N/A | 0.95          | N/A              | N/A               | N/A                 | 2014  [80] |     |
| n-Butylamine   | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.13    | 1.95          | 2.0 20.1        | N/A | 0.95          | N/A              | N/A               | N/A                 | 2014  [81] |     |
| TMAH           | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.13    | 1.95          | 2.0 20.1        | N/A | 0.95          | N/A              | N/A               | N/A                 | 2014  [82] |     |
| Air            | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.12    | 0.01          | 1.85 | 1.9 1.0         | N/A              | N/A               | N/A                 | 2014  [83] |     |
| O₂             | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.12    | 0.01          | 1.85 | 1.9 1.0         | N/A              | N/A               | N/A                 | 2014  [84] |     |
| N₂             | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.12    | 0.01          | 1.85 | 1.9 1.0         | N/A              | N/A               | N/A                 | 2014  [85] |     |
| Ar             | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.12    | 0.01          | 1.85 | 1.9 1.0         | N/A              | N/A               | N/A                 | 2014  [86] |     |
| CsBr           | Spin coating | ITO/NiOx/PCBM/BCP/Al                                  | N/A        | 0.12    | 0.01          | 1.85 | 1.9 1.0         | N/A              | N/A               | N/A                 | 2014  [87] |     |
have rough and uneven morphologies. To overcome this drawback, various studies have been conducted, which especially focused on surface modification. Among these studies, the research works on dual-functional organic materials, which can not only alleviate the roughness of NiO thin films but also passivate the defects of perovskite layer, have shown meaningful results. It has led to the establishment of an important concept of p-type organic material design suitable for PSCs.

4. Applications of NiOx Thin Film to Perovskite-Based Tandem Solar Cells

Multijunction solar cells, which consist of multiple light-absorbing materials having dissimilar bandgaps, have shown prospective in their PCEs beyond the Shockley–Queisser (S–Q) efficiency limit (single junction based), due to their absorption in the wide wavelength range. From the theoretical calculation, ≈46%, ≈50%, and ≈65% efficiencies were estimated from double-junction, triple-junction, and infinite-junction cells, respectively.[141–143] The PSC is one of the best suitable candidates for the subcell of multijunction structures because of its exceptional properties like tunable bandgap, high structure tolerance, reducing the lattice mismatch at the interface, and high-defect tolerable limit, that originate from its intrinsic defects, mainly lying at the shallow level of valance band and conduction band.[144] Moreover, long electron–hole diffusion lengths (>1 μm) and minority carrier lifetime (>1 μs) are advantageous for high carrier mobility,[145] and its high absorption coefficient (1.5 × 105 cm−1 at 550 nm) is beneficial to reduce its material cost.[146] As a partner of PSCs in double-junction tandem solar cell (TSC) structures, perovskite having different bandgaps, silicon (Eg = 1.12 eV) and copper indium gallium selenide (Eg = 1.1 eV), have been widely investigated, and a tandem cell built on a compound semiconductor gallium arsenide (GaAs) was recently demonstrated by our research group.[147–149] In this section, we especially focus on the TSC devices, which are composed of NiOx-based PSCs, and the role of NiOx in those TSCs will be discussed.

4.1. Perovskite/Si Tandem Solar Cells

Silicon is one of the most widely studied materials as a photoabsorber of bottom cells, because it has suitable bandgap, stability, huge market shares, and low manufacturing cost at the industrial scale.[150,151] The maximum efficiency of Si-based solar cell, reported until now (26.7%), is close to its theoretical efficiency limit (about 29%), and thus to further improve its performance is challenging.[142–144] In this context, the TSC architecture, which integrates the emerging PSCs as a top cell on the Si bottom cell, has brought a new opportunity that can enhance the efficiency of Si solar cell. This approach is also considered as one of the fastest routes to commercialize the PSC technology.[155]

The maximum efficiency of perovskite/Si TSCs was 29.1% in 2020, which is higher than that of each Si and PSC.[152,154] and, recently, even perovskite/perovskite/Si triple-junction solar cells were also demonstrated for optimal light management.[157] The perovskite/perovskite double junction was built on a textured crystalline silicon at the bottom, designed for enhancing light trapping and minimizing light reflection; a high Voc of 2.69 V was achieved. In this structure, 2,2′,7,7′-tetra(N,N-di-tolyl) amino-9,9-spiro-bifluorene (spiro-TTB) was thermally deposited as HTL of the middle cell, but it cannot be utilized as an HTL of the top cell. To form a perovskite layer, cesium bromide (CsBr) and lead iodide (PbI2) were coevaporated as a template layer on spiro-TTB layer, and then formamidinium iodide (FAI) solution was spin coated on the template, which was followed by thermal annealing for the perovskite crystal structure formation. Because the spiro-TTB layer was shown to dewet the transparent

| Table 5. Continued. |
|---------------------|
| **Dopant** | **Method** | **Device configuration** | **Area** [cm²] | **Voc** [V] | **Jsc** [mA cm⁻²] | **FF** | **Initial PCE [%]** | **Retained PCE [%]** | **Storage condition** | **Storage time [days]** | **Year** | **Ref.** |
| Ethylphosphonic acid | Spin coating | ITO/NiO<sub>x</sub>/C<sub>30</sub>FA<sub>2</sub>MA<sub>2</sub>Pb(1<sub>0.75</sub>B<sub>0.25</sub>)<sub>3</sub>/PCBM/BCP/Ag | N/A | 1.03 | 19.50 | 65.0 | 13.0 | 0.50 | Inert gas/75 °C | 0.51 | 2020 | [193] |
| 4-Bromo benzoic Acid | Spin coating | ITO/NiO<sub>x</sub>/C<sub>30</sub>FA<sub>2</sub>MA<sub>2</sub>Pb(1<sub>0.75</sub>B<sub>0.25</sub>)<sub>3</sub>/PCBM/BCP/Ag | N/A | 0.99 | 17.70 | 72.0 | 12.6 | 0.50 | Inert gas/75 °C | 0.55 | 2020 | [193] |
| Adenine | Spin coating | FTO/NiO<sub>x</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PCBM/PEI/Ag | N/A | 1.06 | 22.90 | 77.7 | 18.96 | 0.90 | 50–60 RH/25 °C (w/o encapsulation) | 25 | 2020 | [194] |
| DPI | Spin coating | ITO/NiO<sub>x</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PCBM/BCP/Ag | N/A | 1.04 | 22.90 | 78.0 | 18.6 | N/A | N/A | N/A | 2020 | [195] |
| DNI | Spin coating | ITO/NiO<sub>x</sub>/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PCBM/BCP/Ag | N/A | 1.09 | 23.80 | 78.0 | 20.30 | 0.90 | Ambient air/25 °C (50 nm Al<sub>2</sub>O<sub>3</sub> encapsulation) | 20.8 | 2020 | [195] |
Conductive oxides during the annealing of the perovskite, 30 nm-thick NiOₓ, deposited by the sputtering process, was utilized as an HTL of the top cell. This is due to the advantage of NiOₓ that can form a stable and uniform layer even on the textured structure by properly selecting the deposition method.

### 4.2. Perovskite/CIGS Tandem Solar Cells

Other than Si, copper indium gallium diselenide (CIGS) has been widely investigated as a tandem partner of perovskite due to its suitable bandgap, high absorption coefficient for bottom cell, and high efficiency. In addition, the bandgap of CIGS is tunable in the range of 1.00–1.70 eV by modulation of the [Ga]/([Ga]+[In]) ratio. The maximum reported efficiency of CIGS solar cell is 23.35% along with high stability and cost-effectiveness. Both perovskite and CIGS layers can be prepared in a thin-film format, and thus perovskite/CIGS TSCs are feasible to the flexible solar cell, which has potential in building integrated PVs and mobile devices.

Jost et al. demonstrated a perovskite/CIGS TSC, of which a perovskite top cell was fabricated on a rough CIGS bottom cell. To avoid potential shunting due to the rough surface of CIGS, an ultrathin and uniform NiOₓ layer is formed by ALD method on the front contact of the CIGS cell. The uniformly covered ALD-NiOₓ prevented direct contact between perovskite and ZnO:Al. In addition, PTAA layer was introduced on the interface between NiOₓ and perovskite to reduce the interface recombination losses by forming organic/inorganic bilayer-type HTLs, as explained in the cases of single-junction PSCs earlier.

### 4.3. Perovskite/GaAs Tandem Solar Cells

III–V compound semiconductors (e.g., GaAs) have various advantages over the conventional c-Si such as low-light performance, high efficiency, and small temperature coefficient, but their high production cost has limited their commercialization. Recently, we first demonstrated perovskite/GaAs TSCs, in which the conventional InGaP top cell was replaced with wide-bandgap (>1.82 eV) perovskite PV cells. For this purpose, a solvent-evaporation-controlled process that could provide a light-stable uniform wide-bandgap perovskite was newly developed. One of the main advantages of this TSC approach is that it can improve the usability of compact semiconductor-based PV technology with enhanced performance without significant cost increase for the applications, in which lightweight and flexibility are essential. To construct a PSC structure on the flexible bottom cell, solution-processible NiOₓ NP HTL prepared by the solvothermal method, was utilized for preventing the thermal degradation of the bottom cell.

### 4.4. All-Perovskite Tandem Solar Cells

Because bandgaps of perovskites can be easily tuned by controlling stoichiometries of components, all-perovskite TSCs, composed of perovskites having different bandgaps, have been extensively investigated. Especially, this approach is beneficial to realize high-performance TSCs with low manufacturing cost on flexible substrates. The highest PCEs of all-perovskite TSCs, reported until now, are 25.6% and 24.2% for 0.049 and 1 cm², respectively, and the solution-processed NiOₓ nanocrystal film was utilized as HTL of the wide-bandgap perovskite bottom cell of the TSC. The surface of NiOₓ thin film was further modified with a spin-cast ultrathin (∼5 nm) organic layer, which was a thermally cross-linkable small molecule, N4,N4’-di(naphtalen-1-yl)-N4,N4’-bis(4-vinylphenyl)biphenyl-4,4’-diamine (VNBP), and this modification increased the Voc of solar cell by ≈30 mV due to faster hole extraction and reduced interfacial nonradiative recombination. In addition, the VNBP could change the characteristics of NiOₓ surface, which resulted in a more uniform perovskite layer on VNBP-modified NiOₓ thin film. Meanwhile, a solution-processed all-perovskite triple-junction solar cell with Voc of 2.8 V was also demonstrated. In this architecture, although NiOₓ/PTAA bilayer was utilized to reduce the roughness of NiOₓ in middle cell, severe Voc loss was observed due to the roughness of the front subcell. To overcome this issue, conformal coating of HTL of middle cell on the rough surface of front subcell by sputtering, ALD, addition of self-assembled monolayers, and evaporation was suggested.

### 5. Conclusion and Future Outlook

In this Review, we overviewed the approaches to prepare high-performance NiOₓ thin films for p–i–n-structured PSC devices, in which contents are mainly about 1) their synthetic methods including both solution- and vacuum-assisted processes, 2) modification of their properties with dopants and functional materials, and 3) application of NiOₓ thin films to perovskite TSCs.

In general, NiOₓ has various potential advantages as HTM of PSCs compared with other inorganic and organic HTMs: a well-aligned energy band with VBM of perovskite absorbers, fairly high electrical conductivity with proper hole mobility, high transmittance, low-temperature processibility, and cost-effectiveness. However, it also has shortcomings such as poor morphology, especially severe in solution-processed thin films. In planar p–i–n-structured PSCs, the properties of HTMs as the bottom layer have a profound effect on the quality of following perovskite layer. To figure out this issue, a variety of methods (i.e., solvothermal, combustion, PLD, e-beam, and ALD) have been applied to fabricate more denser, compact, and highly crystallized NiOₓ thin films. For further strengthening its merits, diverse methods such as doping of various types of metals (i.e., transition metals, alkali metals, alkaline metals, rare earth metals, and multimetals) and functionalization using organic materials have been widely studied. Among these, external doping significantly influences its optical and electrical properties by modifying its stoichiometry, oxidation states, and band structure and thus, enhancement in conductivity, transmittance, and work function. Those doping elements also affect structural properties, which improve the surface morphology and passivate the trap states. As for the surface functionalization with organic materials, the defects can be suppressed and its optical and electrical properties can be improved toward high-performance and stable planar PSCs. Those molecules behave as anchoring agents and form covalent bonds with the unsaturated atoms, decreasing the defect density at the
interface between NiO$_x$ and perovskite, which can enhance the carrier extraction and blocking capability.

NiO$_x$ is an efficient and cost-effective material with high stability, but NiO$_x$-based PSCs have various limitations to achieve high efficiency. As approaches to go beyond these limitations, we summarized various advanced fabrication and modification strategies here to resolve its disadvantages and further enhance its merits as a high-performance HTM of planar PSCs. Based on this Review, we suggest several strategies and outlooks for the application of NiO$_x$ to the PSC devices. First, an appropriate synthesis method should be selected after considering device area and uniformity, required for the devices. A solution-based spin-casting process at low temperatures is commonly utilized to form NiO$_x$ thin film, but it is unsuitable for large-area devices and often induces nonuniform surface. As discussed in this Review, various physical and chemical deposition methods such as electrodeposition, PLD, e-beam deposition, ALD, and sputtering deposition can be also applied to fabricate high-quality NiO$_x$ thin films on large-area devices.

Second, the strategies to modify the properties of NiO$_x$ should be considered. One of the most crucial goals of the solar cell devices is to produce higher efficiency under the same light environment. To achieve this goal, we can apply various approaches such as doping of HTL, passivation of perovskite layer through functional materials, and stabilization of the interface between HTL and perovskite. Especially for NiO$_x$ HTLs, doping could be an efficient way that can dramatically enhance the efficiency of PSCs by increasing its conductivity as well as adjusting its energy level. Therefore, it is essential to optimize the type and concentration of the dopant after considering the characteristics of pristine NiO$_x$ and the composition of perovskite. A bilayer-type HTL, composed of inorganic NiO$_x$ and p-type organic semiconductor, could be an effective approach for improving the PV parameters of the device. Organic materials could improve the morphology of NiO$_x$ and their functional groups could be utilized for passivating defects of perovskite such as undercoordinated Pb$^{2+}$ and halide vacancies. To maximize these effects, the design of organic materials and their application to an interface between inorganic HTL and perovskite should be carefully considered.

NiO$_x$ is a promising material for HTLs of PSCs in terms of efficiency, stability, and economics. Due to its relatively simple structure, it is also convenient to synthesize and dope, compared with other types of HTLs. Especially, this is feasible for multijunction PSCs, which are expected as one of the fastest routes to commercialize PSC technology. From this point of view, we believe that the application of NiO$_x$ layer to solar cell devices could be close to commercialization. To go a step further, a future study should be focused on not only the improvement of device efficiency but also the optimization of its parameters in thin-film format for the mass production of flexible PSCs.

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Conflict of Interest

The authors declare no conflict of interest.

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hole transport materials, inorganic materials, nickel oxide, perovskite solar cells, processing methods

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