

# Perovskite solar cells with NiO<sub>x</sub> hole-transport layer

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**Citation:** M J Li, Z L Zhang, J Sun, F Liu, J Z Chen, L M Ding, and C Chen, Perovskite solar cells with NiO<sub>x</sub> hole-transport layer[J]. *J. Semicond.*, 2023, 44(10), 100201. <https://doi.org/10.1088/1674-4926/44/10/100201>

Inverted perovskite solar cells (PSCs) have attracted interest due to their simple fabrication, long-term stability, and small hysteresis<sup>[1-3]</sup>. It is noteworthy that the quality of the hole-transport layer (HTL) largely determines the device performance. Nickel oxide (NiO<sub>x</sub>) has been paid great attention as a hole-transport material in PSCs because of its natural p-type property, low cost, good stability, and high transmittance<sup>[4, 5]</sup>. Further, NiO<sub>x</sub> has a suitable bandgap ( $E_g > 3.50$  eV) and a well-matched valence band with perovskites, which is conducive to hole collection and electron blocking<sup>[6, 7]</sup>. NiO<sub>x</sub>-based inverted PSCs are promising for flexible and tandem solar cells due to their negligible hysteresis and low processing temperatures compatible with flexible substrates. Thus, more investigations into surface/interface modification, bandgap alignment, and the physical principles are worth paying effort to enhance device performance further.

Sol-gel method is mainly used to prepare Ni(OH)<sub>2</sub> by reacting Ni(NO<sub>3</sub>)<sub>2</sub> with NaOH and then calcination to obtain NiO<sub>x</sub> nanoparticles (Fig. 1(a))<sup>[8]</sup>. However, NO<sub>3</sub><sup>-</sup> as residue cannot be removed by subsequent process. They will be embedded in Ni(OH)<sub>2</sub>, thus reducing the efficiency and long-term stability of the device. These ions can be removed at high temperatures, but this will lead to poor dispersion of the generated NiO<sub>x</sub> in solution, seriously affecting the quality of the subsequent NiO<sub>x</sub> HTL. In addition, NiO<sub>x</sub> has a relatively low inherent conductivity, which limits the efficiency enhancement of PSCs<sup>[9]</sup>. At the interface, organoiodide in perovskite can react with Ni<sup>3+</sup> in NiO<sub>x</sub> layer, and this reaction can affect the device stability. As shown in Fig. 1(b), there are three reactions at the interface<sup>[10]</sup>: (1) Oxidation and deprotonation reactions generate iodine vapor and free protons; (2) the formation of volatile products at high temperatures, including hydrogen cyanide (HCN), methyl iodide (CH<sub>3</sub>I) and ammonia (NH<sub>3</sub>); (3) with the increase of vapor pressure of free FA and MA molecules, the condensation product N-methyl formamide can be formed. Therefore, to enhance the intrinsic stability and mobility is necessary for improving the device performance.

Recently, doping ions have become an important strategy for improving NiO<sub>x</sub> conductivity. To increase hole concentration, it is preferred to dope metal cations into NiO<sub>x</sub> as acceptors. Doping metal ions like Li<sup>+</sup><sup>[11]</sup>, Cs<sup>+</sup><sup>[12]</sup>, Ag<sup>+</sup><sup>[13]</sup>, Cu<sup>2+</sup><sup>[14]</sup>, Sr<sup>2+</sup><sup>[15]</sup>, Co<sup>2+</sup><sup>[6]</sup>, Zn<sup>2+</sup><sup>[16]</sup>, rare earth ions<sup>[17]</sup> or Pb<sup>2+</sup>/Li<sup>+</sup><sup>[18]</sup> can effectively improve NiO<sub>x</sub> conductivity. Chen *et al.* doped Cs<sup>+</sup> into NiO<sub>x</sub> to increase conductivity and workfunction, resulting in a significant improvement in efficiency and stability<sup>[12]</sup>. Doping bivalent metal cations with the same valence state as Ni can improve the mobility of NiO<sub>x</sub> and device efficiency. Fig. 2(a) shows that the ionic radii of common bivalent metal cations mismatch with Ni ion radius within 10%, which can effectively promote the occurrence of substitution<sup>[19]</sup>. Dong *et al.* used KBr as a buffer layer between the perovskite and NiO<sub>x</sub> to improve the valence band maximum of NiO<sub>x</sub> to -5.37 eV, which matches better with perovskite and facilitates charge separation<sup>[20]</sup>. Chen *et al.* made facile NiO<sub>x</sub> modification by KCl to synchronously suppress interfacial recombination and ion migration<sup>[21]</sup>.

The interfacial recombination loss and mismatched band alignment limit the performance enhancement of inverted PSCs. Though doping metal cations could improve the conductivity of NiO<sub>x</sub> layer, the impurity ions cannot be avoided. In response, Wang *et al.* used [BMIm]BF<sub>4</sub> ionic liquid (IL) assisted synthesis to prepare high-quality NiO<sub>x</sub> nanoparticles<sup>[22]</sup>. [BMIm]BF<sub>4</sub> is added before the reaction of Ni(NO<sub>3</sub>)<sub>2</sub> with NaOH (Fig. 2(b)). The multifunctional substitution of imidazole rings produces more chemical bonds. In addition, cations can inhibit the adsorption of impurity ions on Ni(OH)<sub>2</sub>, thus obtaining NiO<sub>x</sub>-IL HTL with high conductivity. Yang *et al.* used TTTS as a chelating agent of Ni<sup>2+</sup> in NiO<sub>x</sub> layer to improve its conductivity<sup>[23]</sup>. TTTS and Ni<sup>2+</sup> are combined by strong Ni<sup>2+</sup>-N coordination bonds in NiO<sub>x</sub>, increasing the ratio of Ni<sup>3+</sup> : Ni<sup>2+</sup> (Fig. 2(c)). The increase of Ni<sup>3+</sup> content adjusted the band structure of NiO<sub>x</sub>, thereby increasing the hole density and mobility, resulting in enhanced PCE over 22%. Carbon materials with good conductivity are also suitable modifiers for NiO<sub>x</sub>. Yin *et al.* developed a NiO<sub>x</sub>/Carbon heterostructure (Fig. 2(d)) as an interlayer for fabricating efficient PSCs with good interfacial energy level alignment and more efficient charge transport<sup>[24]</sup>.

The interfacial lattice mismatch and adverse reactions in NiO<sub>x</sub>-based PSCs cannot be ignored. Self-assembled molecu-

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Received 5 SEPTEMBER 2023.

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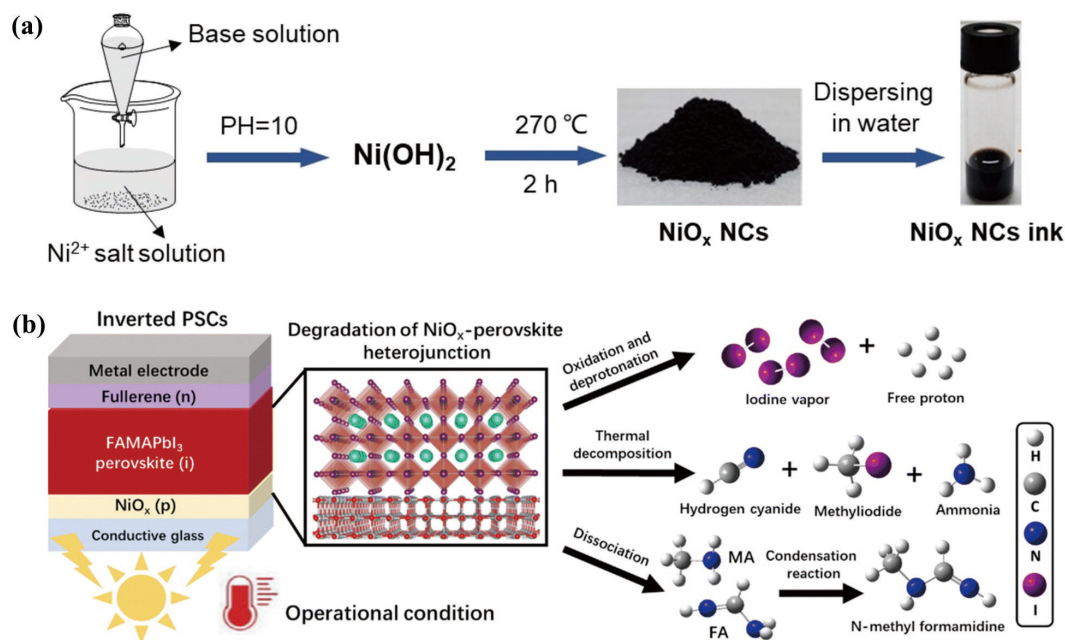


Fig. 1. (Color online) (a) Sol-gel preparation of  $\text{NiO}_x$  nanoparticles. Reproduced with permission<sup>[8]</sup>, Copyright 2023, Wiley. (b) Possible degradation mechanism of  $\text{NiO}_x$ -perovskite heterojunction. Reproduced with permission<sup>[10]</sup>, Copyright 2022, the Royal Society of Chemistry.

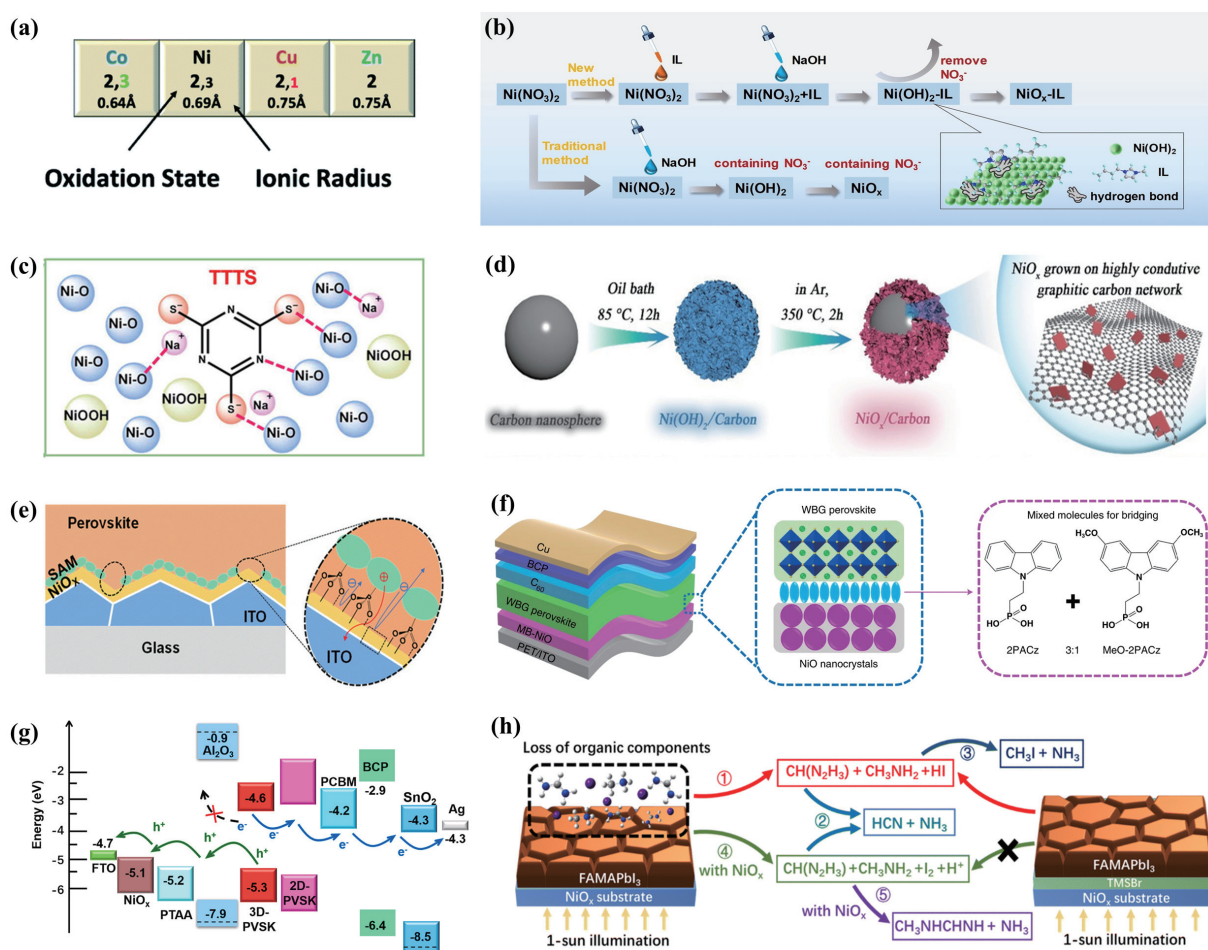


Fig. 2. (Color online) (a) The oxidation state and ionic radius for several metals. Reproduced with permission<sup>[19]</sup>, Copyright 2020, the Royal Society of Chemistry. (b) Synthesis of  $\text{NiO}_x$  nanoparticles. Reproduced with permission<sup>[22]</sup>, Copyright 2022, Wiley. (c)  $\text{NiO}_x$  modified by TTTs. Reproduced with permission<sup>[23]</sup>, Copyright 2022, Wiley. (d) The preparation of  $\text{NiO}_x$ /carbon heterostructure. Reproduced with permission<sup>[24]</sup>, Copyright 2021, Wiley. (e) SAM-modified  $\text{NiO}_x$  at the interface. Reproduced with permission<sup>[27]</sup>, Copyright 2021, Wiley. (f) Flexible PSCs with bridging molecules. Reproduced with permission<sup>[28]</sup>, Copyright 2022, Nature. (g) The energy level diagram for device with PTAA. Reproduced with permission<sup>[30]</sup>, Copyright 2021, Elsevier. (h) TMSBr buffer layer inhibiting perovskite degradation. Reproduced with permission<sup>[10]</sup>, Copyright 2022, the Royal Society of Chemistry.

lar layers (SAMLs) are effective carrier-transport layers in PSCs due to their unique ability to manipulate interface properties as well as their simple processing and scalable manufacturing<sup>[25]</sup>. However, the defects and pinholes caused by its adsorption process can seriously degrade device performance. Therefore, SAMLs are often combined with hole-transport materials such as NiO<sub>x</sub> to improve hole transport. The phosphoric acid (PA) group in 2PACz has a strong coordination with NiO<sub>x</sub><sup>[26]</sup>, and it is easier to spin-coat 2PACz onto NiO<sub>x</sub> layer. The presence of 2PACz can promote the crystallization of perovskite and regulate the bandgap of perovskite. Sun *et al.* found that tridentate binding between MeO-2PACz and NiO<sub>x</sub> is superior to the double-toothed binding between MeO-2PACz and ITO (Fig. 2(e))<sup>[27]</sup>. This close contact reduces defects and pinholes at the interface, thereby improving device performance. In 2022, Li *et al.* used a mixture of 2PACz and MeO-2PACz as a molecular bridge at the interface to reduce interface recombination and they can act as a stress buffer layer at the interface to improve the bending durability of the flexible device (Fig. 2(f))<sup>[28]</sup>. Recently, Zhang *et al.* used *p*-chlorobenzenesulfonic acid (CBSA) self-assembly to anchor NiO<sub>x</sub> and perovskite crystals, where the chlorine end can provide a growth site for perovskite and also release the interfacial strain<sup>[29]</sup>. The sulfonic acid group in CBSA can passivate the surface defects of NiO<sub>x</sub>, which is conducive to carrier extraction.

Besides SAMLs, introducing long-chain organic molecules can also improve surface properties for bandgap alignment and charge transfer. PTAA can act as a molecular bridge. Fig. 2(g) shows that the valence band of PTAA (−5.2 eV) is very close to the valence band of NiO<sub>x</sub> (−5.1 eV) and perovskite (−5.3 eV), which can quickly transfer holes from perovskite to NiO<sub>x</sub><sup>[30]</sup>. Recently, Li *et al.* obtained a PCE of 25.12% (certified 24.6%) for inverted NiO<sub>x</sub>-based PSCs by using NiO<sub>x</sub>/PTAA/Al<sub>2</sub>O<sub>3</sub> as hole-transport layer<sup>[31]</sup>. To eliminate multi-step photochemical reactions at the interface, Wu *et al.* constructed an aprotic trimethyl bromosulfonic acid (TMSBr) buffer layer at NiO<sub>x</sub>/perovskite interface (Fig. 2(h))<sup>[10]</sup>. TMSBr has excellent photothermal stability, and strong trap-passivation capability. The T<sub>80</sub> lifetime for the device under AM1.5G light is 2310 h.

## Acknowledgments

This work was supported by the National Natural Science Foundation of China (62004058 and U21A2076), Natural Science Foundation of Hebei Province (F2020202022), State Key Laboratory of Reliability and Intelligence of Electrical Equipment (EERI\_PI20200005), S&T Program of Hebei (215676146H and 225676163GH), and Hebei Graduate Innovation Funding Project (CXZZBS2023037 and CXZZSS2023026). L. Ding thanks the National Key Research and Development Program of China (2022YFB3803300), the open research fund of Songshan Lake Materials Laboratory (2021SLABFK02), and the National Natural Science Foundation of China (21961160720).

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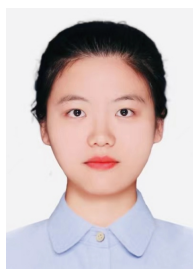
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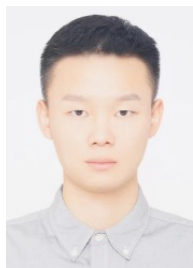
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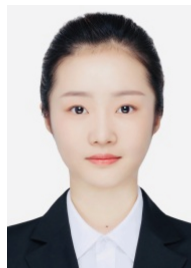
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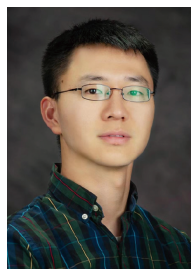
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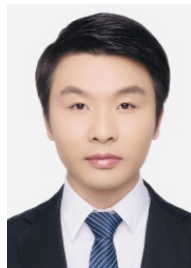
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