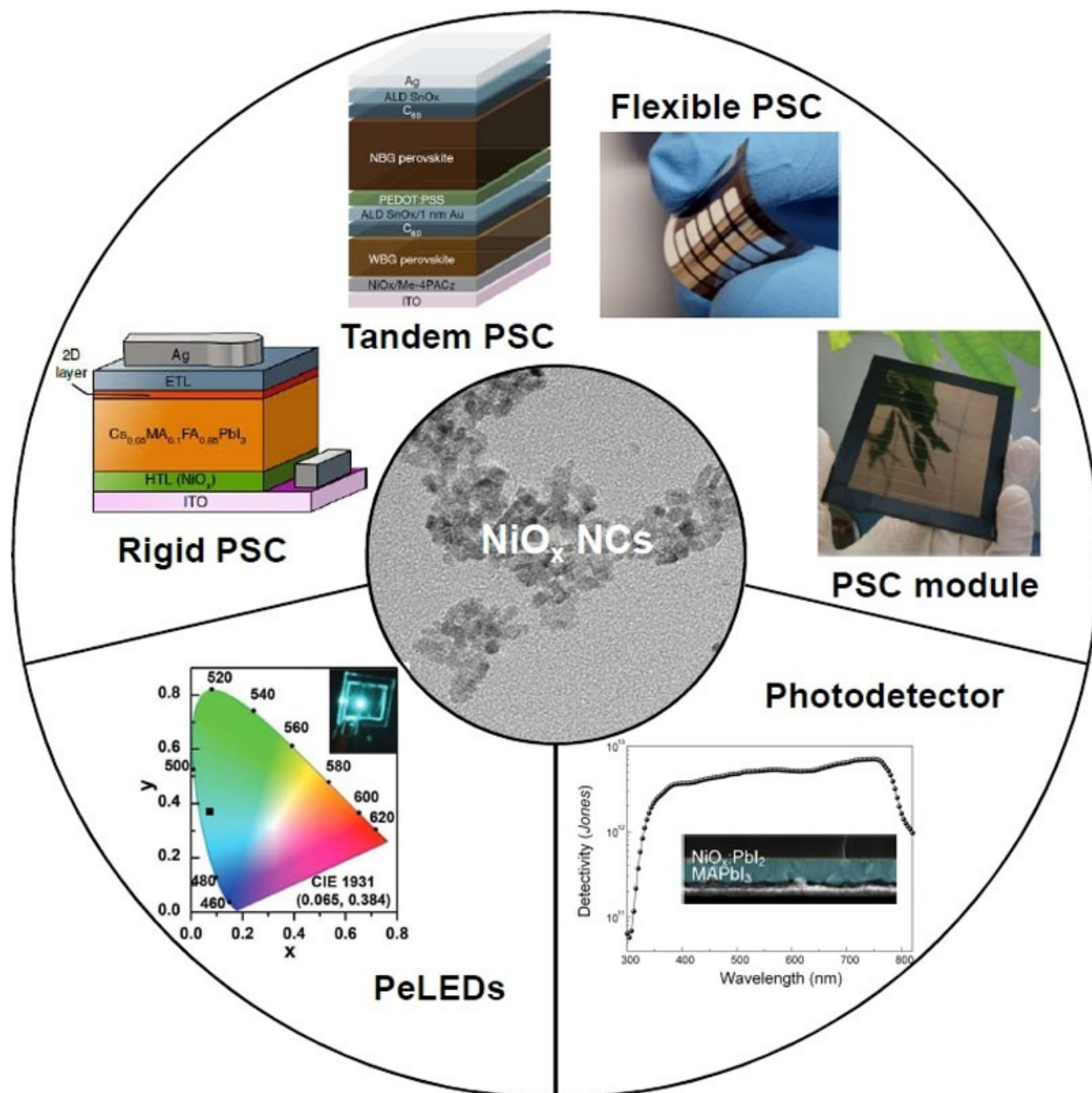


Perovskite Solar Cells

Dopant-free NiO_x Nanocrystals: A Low-cost and Stable Hole Transport Material for Commercializing Perovskite OptoelectronicsHong Zhang⁺,* Chenxu Zhao⁺, Jianxi Yao, and Wallace C. H. Choy*

Abstract: Advancing inverted (p-i-n) perovskite solar cells (PSCs) is critical for commercial applications given their compatibility with different bottom cells for tandem photovoltaics, low-temperature processability ($\leq 100^\circ\text{C}$), and promising operational stability. Although inverted PSCs have achieved an efficiency of over 25 % using doped or expensive organic hole transport materials (HTMs), their synthesis cost and stability still cannot meet the requirements for their commercialization. Recently, dopant-free and low-cost non-stoichiometric nickel oxide nanocrystals (NiO_x NCs) have been extensively studied as a low-cost and effective HTM in perovskite optoelectronics. In this minireview, we summarize the synthesis and surface-functionalization methods of NiO_x NCs. Then, the applications of NiO_x NCs in other perovskite optoelectronics beyond photovoltaics are discussed. Finally, we provide a perspective for the future development of NiO_x NCs for the commercialization of perovskite optoelectronics.

1. Introduction

Perovskite solar cells (PSCs) have attracted intensive attention owing to their low-cost fabrication, excellent electronic properties, and superior performance.^[1–10] Particularly, advancing inverted (p-i-n) PSCs is critical for their commercial applications given their compatibility with different bottom cells for tandem photovoltaics,^[11–14] low-temperature processability ($\leq 100^\circ\text{C}$),^[15] and promising operational stability.^[16,17] Recently, an increasing global effort has been invested to advance inverted PSCs, and most of the endeavors have been focused on compositional engineering,^[18] additive engineering,^[19] processing methods,^[20–22] and interfacial engineering.^[8,23–27] Although the champion power conversion efficiency (PCE) of inverted PSCs has exceeded 25 %, doped or expensive organic hole transport materials (HTMs), such as poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) (PTAA) and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), were initially employed to achieve high performance. Although organic HTMs have been utilized in the highest efficiency of p-i-n structure PSCs, their drawbacks such as high fabrication cost and poor wetting capacity, which hinder their large-scale applications towards commercialization. Alternatively, various inorganic p-type semiconductors (e.g., CuSCN ,^[28] NiO_x ,^[29,30] and Cu_2O)^[31] could replace these organic HTMs for inverted PSCs because of their high stability and intrinsically high carrier mobility and conductivity. Among them, dopant-free NiO_x has been extensively investigated as inorganic HTM for inverted

PSCs owing to its advantages of wide band gap (> 3.5 eV) and energetically favorable energy level alignment with most perovskite absorbers and stable chemical properties.

Traditionally, NiO_x films can be grown with a wide range of deposition techniques, such as sputtering,^[32] pulsed laser deposition (PLD),^[33] atomic layer deposition (ALD),^[34] and sol-gel coating.^[29,35,36] However, all of the reported NiO_x films require sophisticated conditions such as high-temperature (300 – 500°C) thermal annealing and/or high vacuum procedures during the fabrication process. Such stringent conditions increase the fabrication cost and hinder their practical uses. The high annealing temperature will also make the fabrication of devices on flexible substrates difficult. To address these challenges, our group invented a simple chemical precipitation method to synthesize highly crystalline and dopant-free NiO_x NCs inks, enabling the preparation of a room-temperature solution-processed hole transport layer (HTL) for high-efficiency inverted PSCs with a PCE of 17.60 % and 14.53 % on rigid and flexible substrates respectively.^[37] Then, dopant-free NiO_x NCs were extensively studied as a low-cost and highly efficient HTM in single-junction and tandem perovskite photovoltaics (Figure 1).^[11–13,17,21,25,38–51] To date, the most efficient NiO_x NCs-based single-junction and tandem PSCs have achieved PCEs of 23.91 %^[25] and 27.40 %, ^[12] respectively. In this minireview, we summarize the synthesis and surface-functionalization methods for NiO_x NCs. Then, the applications of NiO_x NCs in the other perovskite optoelectronics beyond photovoltaics are discussed. Finally, we provide a perspective for the future development of NiO_x NCs promoting the commercialization of perovskite optoelectronics.

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2. Synthesis of dopant-free NiO_x NCs

The synthesis of dopant-free and organic ligand-free NiO_x NCs was first reported by our group using an unprecedented chemical precipitation method (Figure 2).^[37,52] First, the commercially available raw materials of nickel salts and base were easily dissolved in deionized water. After dropwise adding the base solution, the clear green aqueous solution turned turbid. Through accurately controlling the solution pH value to 10, an ultrafine nickel hydroxide $\text{Ni}(\text{OH})_2$ participant was obtained in a considerable yield [Eq. (1)]. The obtained apple green product was dried and calcined at 270°C for 2 h in air to decompose into dark black NiO_x NCs [Eq. (2)]. This calcination procedure is based on the thermal

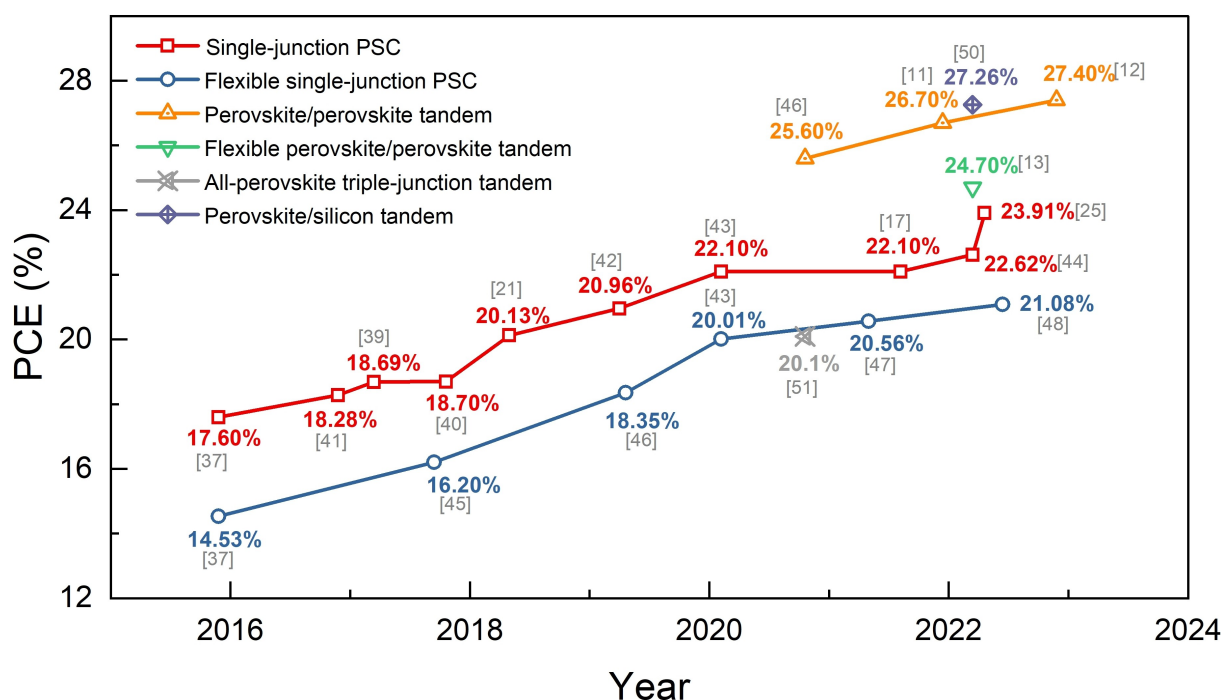


Figure 1. Progress of NiO_x NCs-based PSCs.

decomposition of Ni(OH)₂ to produce dopant-free NiO_x NCs with a diameter of approximately 3–5 nm. The calcination atmosphere has a significant influence on the decomposition of Ni(OH)₂ and the compositions of the resulting

NiO_x NCs.^[53] The product of NiO_x NCs and the corresponding dispersion aqueous inks are shown in Figure 2.



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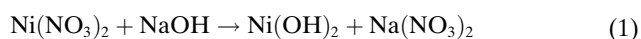


current research interests include: perovskite solar cell materials and devices; semiconductor nanometer photoelectric functional materials and devices.

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The calcination temperature of 270 °C was rationally selected to achieve highly crystalline and dopant-free NiO_x NCs as well as stable colloidal inks. The incomplete decomposition of the byproduct nickel hydroxide ($\text{Ni}(\text{OH})_2$) [see Eqs. (1) and (2)] at temperatures below 270 °C and the poor dispersibility of the NiO_x NCs calcined at temperatures higher than 270 °C were identified as causes of the poor ability of the synthesized NiO_x NCs to form high-quality HTLs.^[52,54]

To further identify the fundamental mechanism, Jaramillo et al. conducted a detailed characterization study of NiO_x NCs and their colloidal dispersions.^[55] As shown by the scanning transmission electron microscopy (STEM) in Figures 3a–c, crystalline NiO_x NCs (bright pixels) were immersed in an amorphous interconnected phase, which is relevant to the formation of stable colloidal dispersions. This amorphous interconnected phase strongly diminished with the increasing calcination temperature of $\text{Ni}(\text{OH})_2$ from 270 °C to 330 °C. Although the increase of synthesis temperature can improve the overall crystallinity, the NiO_x NCs synthesized at 330 °C have poor dispersion stability in solution and will precipitate rapidly, which is caused by the removal of $\text{Ni}(\text{OH})_2$ trace, indicating that the central role of OH^- groups in stabilizing the NiO_x dispersion. The optimal synthesis temperature of NiO_x NCs is 270 °C, which will cause a small amount of unreacted $\text{Ni}(\text{OH})_2$ and NO_3^- in the final product. The thermogravimetric analysis (TGA), Fourier transform infrared (FTIR), and in situ Raman spectroscopy characterization of the NiO_x NCs show the presence of some reaction byproducts in the amorphous phase, especially nitrates, hydroxide and sodium (Figures 3d–g). These byproducts in the amorphous phase have a relevant role in the stabilization of the colloidal dispersion of NiO_x

NCs and ensure connectivity in the final deposited compact film.

As discussed above, the amorphous phase plays a critical role in stabilizing the colloidal dispersion of NiO_x NCs and the morphological quality of the formed film. Different synthesis routes have also been developed to control the formation dynamics and minimize the surface defects of NiO_x NCs. In the following sections, we will discuss the critical factors that affect the dispersion and film quality of the synthesized NiO_x NCs from three aspects of base, nickel salts, and additives.

2.1. Bases

In the reaction shown in equation 1, since NaOH is a strong base, the pH value of 10 during the precipitation process should be precisely controlled to obtain well-dispersed NiO_x NCs. Recently, other precipitation methods have been reported for the stable mass production of highly disperse NiO_x NCs by replacing NaOH with other soft bases. Tai et al. reported the use of ammonia as a soft base for the precipitation process and systematically studied the influence of the amount of ammonia addition on the crystallinity, particle size, and yield of the NiO_x NCs.^[56] They found that highly dispersed NiO_x NCs could be readily synthesized with considerable yield under a wide pH window from weak acidic ($\text{pH} \approx 5.5$) to weak basic ($\text{pH} \approx 9$). The as-prepared NiO_x NCs were used as HTMs for fabricating efficient FASnI_3 -based lead-free PSCs with a PCE of $\approx 8\%$. Recently, organic base with a tunable cation structure has been reported to synthesize NiO_x NCs with tunable sizes and energy levels. For example, using tetraalkylammonium hydroxides (TAAOHs, alkyl = methyl, ethyl, propyl, butyl) as precipitating bases, the particle size of the NiO_x NCs depends strongly on the alkyl chain length of TAAOHs and the average particle size can be gradually tuned from 4.04 nm to 2.13 nm by altering the alkyl chain from methyl group to butyl group. This phenomenon could be under-

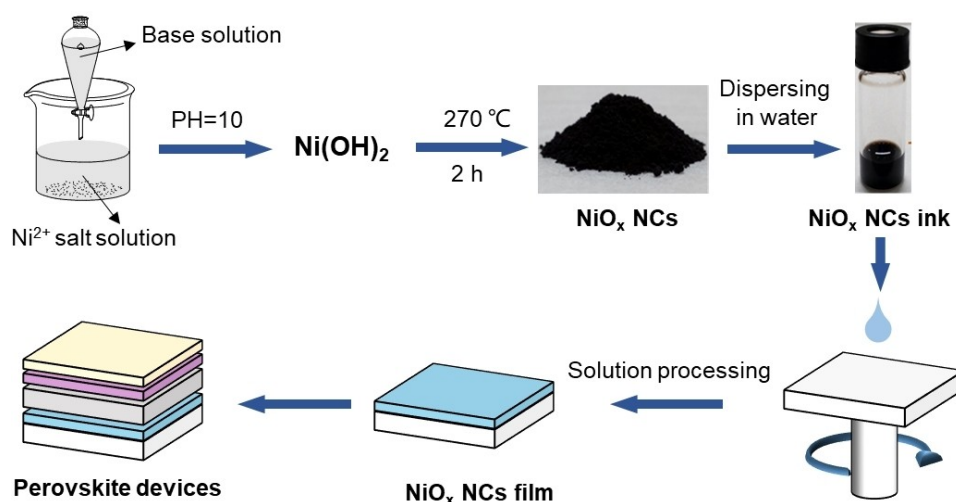


Figure 2. Schematic illustration of the NiO_x NCs preparation, film formation and the relevant device fabrication.

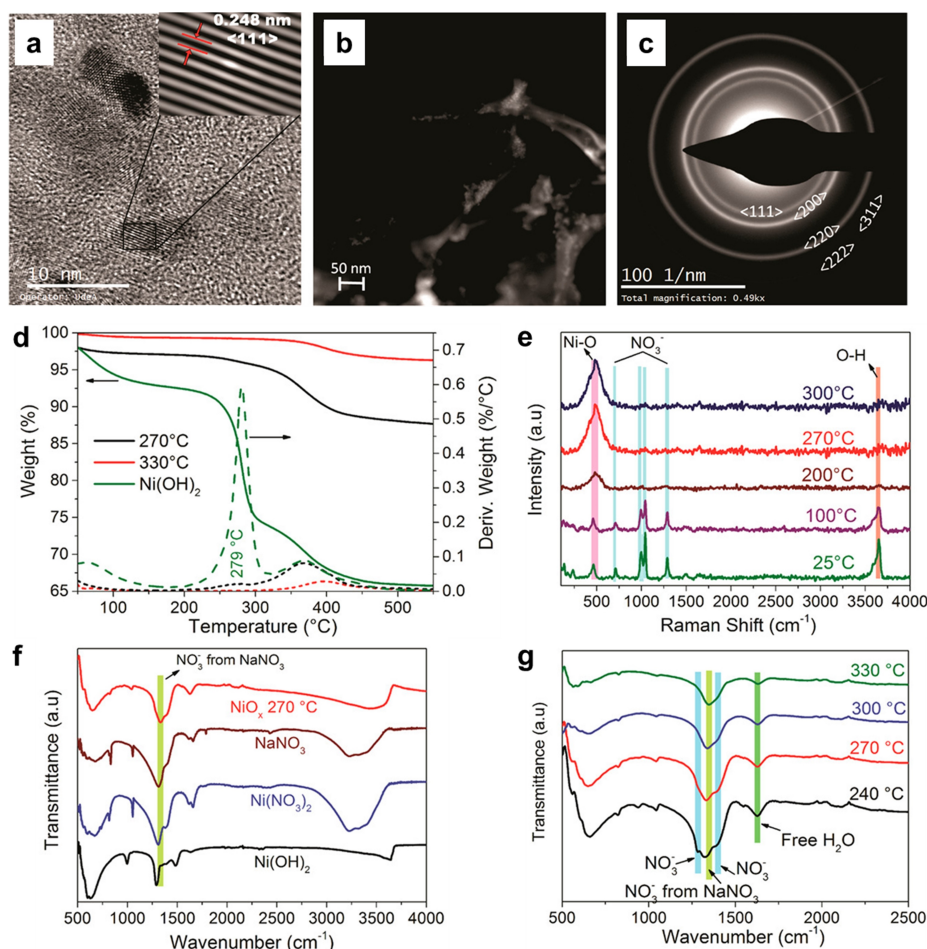


Figure 3. Characterizations of synthesized NiO_x NCs. a) HRTEM analysis reveals crystalline NiO_x NCs sized below 5 nm. b) STEM enabled identifying a crystalline NiO_x phase (bright pixels) immersed in an amorphous interconnected phase. c) Corresponding diffraction pattern of the NiO_x NCs confirming the presence of crystalline and amorphous NiO_x phases. d) TGA curves for the precipitated $\text{Ni}(\text{OH})_2$ and the NiO_x NCs obtained at 270 and 330 °C. e) Raman in situ for the conversion of $\text{Ni}(\text{OH})_2$ to NiO_x . f) FT-IR spectra of the possible compounds present as byproducts of the synthesis of NiO_x NCs. g) FT-IR spectra of NiO_x NCs obtained at different temperatures indicating the loss of NO_3^- ions. Adapted with permission from Ref. [55].

stood in two ways: (i) The alkalinity of the TAAOHs decreases with the increase of the alkyl chain length from ethyl to butyl, deceleration the growth rate of the $\text{Ni}(\text{OH})_2$ precipitates;^[57] (ii) The steric effect caused by the bulky cation becomes prominent as the alkyl chain length increases, which will also leads to the reduced growth rate of the $\text{Ni}(\text{OH})_2$ precipitates.^[57,58] These two reasons eventually determine the size of the final NiO_x NCs after the decomposition of $\text{Ni}(\text{OH})_2$. Meantime, the valence band maximum (VBM) of the corresponding NiO_x NCs shows a downshift trend from -5.04 eV in the methyl case to -5.30 eV in the butyl case due to the different Ni^{3+} contents in the NCs, providing an opportunity to adjust the energy level alignment between the VBM of the NiO_x NCs and the highest occupied molecular orbital of the perovskite to minimize the energy loss for hole injection at the NiO_x /perovskite interface. However, the presence of the Ni^{3+} species at the surface of the NiO_x film is highly detrimental to both the efficiency and photostability of PSCs. After further passivating the detrimental Ni^{3+} species on the

surface of the NiO_x HTL with PTAA, a PCE approaching 23 % was obtained, which is currently one of the highest PCEs reported for NiO_x -based inverted PSCs.

2.2. Nickel salts

The ions in the precursor induce electrostatic interactions between the reactive materials, which strongly affect the morphology of the resulting NiO_x NCs. Therefore, the role of anions in nickel salts in the morphological evaluation during the synthesis of NiO_x NCs has been investigated.^[59] Three nickel salts, namely, $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were selected as raw materials to prepare NiO_x NCs using the chemical precipitation method.^[37,52] The resulting NCs are noted as $\text{NiO}_x\text{-Ac}$, $\text{NiO}_x\text{-NO}_3$ and $\text{NiO}_x\text{-Cl}$, respectively. All the newly prepared NiO_x NCs can be uniformly dispersed in water and show a pure black color. Notably, no obvious agglomeration and layering can be observed in the $\text{NiO}_x\text{-NO}_3$ ink even after one month.

By contrast, the $\text{NiO}_x\text{-Cl}$ solution appears gray black and irregular in shape, while the $\text{NiO}_x\text{-Ac}$ shows serious precipitation. The NiO_x NCs prepared from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ have excellent dispersity in water and solution stability. The difference in solution stability and dispersion in water of the resulting NiO_x NCs reveals that the as-prepared NiO_x NCs possess different nanoparticle sizes. The average particle size of the $\text{NiO}_x\text{-NO}_3$ ink is approximately 25 nm, while the average sizes of the $\text{NiO}_x\text{-Cl}$ and $\text{NiO}_x\text{-Ac}$ inks are approximately 250 nm and 2.5 nm, indicating the serious aggregation of $\text{NiO}_x\text{-Cl}$ nanoparticles and the precipitation of the large $\text{NiO}_x\text{-Ac}$ nanoparticles. The much smaller and uniform particle size of $\text{NiO}_x\text{-NO}_3$ result in better dispersion in water and stability in solution, which further improve the crystallinity with a sharp and high X-ray diffraction (XRD) peak intensity.

These variations in performance and morphology can be attributed to the three different anions possessing the same valence states of -1 , and different sizes and electrostatic actions, which might lead to adsorption on the precipitates by electrostatic action and influence the precipitation process. Even if the size of these three anions follows the $\text{Ac}^- > \text{NO}_3^- > \text{Cl}^-$ regulation, the as prepared NiO_x NCs show different rules because the Cl^- has strongest electrostatic attractions^[19] with Ni^{2+} . Therefore, the existence of Cl^- leads to the mutual attraction between $\text{Ni}(\text{OH})_2$ particles, resulting in bigger particles. Meanwhile, the loose adhesion of Ac^- on the $\text{Ni}(\text{OH})_2$ particles facilitates aggregation to form a precipitate. NO_3^- anions show the proper electrostatic force on the $\text{Ni}(\text{OH})_2$ clusters, which results in a uniform NiO_x NCs size and well dispersion in water. As a result, the PSC using $\text{Ni}(\text{NO}_3)_2$ fabricated HTL exhibits performance of 18.4 % with good reproducibility and stability, which is much higher than the 16.3 % of PSCs with a NiCl_2 fabricated NiO_x layer. Similarly, Choi reported that NiO_x NCs from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ show more uniform particle shapes with lower sizes and better dispersibility in the solvent than $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, additionally improving the stability and photovoltaic performance of devices.^[60]

2.3. Surface ligand management

Although the existence of ions, such as NO_3^- , can adjust the size of colloidal particles and improve the dispersion and stability in the solution, the impurity of as-prepared NiO_x NCs films with embedded ions is detrimental to the efficiency and long-term stability of the relevant PSCs due to the large number of defects at the perovskite/ NiO_x interface. Li et al. reported that ionic liquid can be employed as an additive in the synthesis process of NiO_x NCs to effectively remove residual ions, presenting a very promising way of synthesizing high-quality NiO_x NCs with good dispersion in the solvent.^[44] Specifically, 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{BMIm}]\text{BF}_4$) was added into the $\text{Ni}(\text{NO}_3)_2$ precursor before reacting with the NaOH aqueous solution. The simulation results show that the low adsorption energy between $[\text{BMIm}]^+$ and $\text{Ni}(\text{OH})_2$ promotes the combination by a strong hydrogen bond, which

inhibits the adsorption of NO_3^- impurity ions and provides an important prerequisite for the subsequent production of NiO_x NCs. The advantages of replacing NO_3^- with the $[\text{BMIm}]^+$ cation are as follows: (i) two-fold increases in the conductivity and hole mobility of NiO_x NCs films, (ii) better energy level matching with perovskite films, and (iii) inhibition of the interfacial degradation reaction at the perovskite/ NiO_x interface. Consequently, ionic liquid modified NiO_x NCs as HTL endowed the hysteresis-free PSC with an efficiency of up to 22.62 % and excellent operational stability. This strategy provides a new understanding of the surface chemistry of NiO_x NCs, which is vital in improving the relevant device performance and stability.

3. Solution processing of NiO_x NC films

Due to the high crystallinity and excellent dispersion in water of NiO_x NCs, the fabrication process of NiO_x film could adopt simple spin-coating or blading process to prepare films with good quality in ambient environment. Meanwhile, different to the traditional sol-gel method, high temperature ($>200^\circ\text{C}$) annealing process doesn't need for the deposition of NiO_x NC films. The as-deposited dopant-free NiO_x NC films possess a large band gap (3.5–3.9 eV) and a deep valence band (VB) around 5.1–5.4 eV, showing good match with various kind of perovskite layers (5.4–5.6 eV).^[45] Benefitting from the large doping of trivalent Ni^{3+} ions, the dopant-free NiO_x NC films have comparable high mobility around $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^[61] which offers it become a highly competitive alternative as HTL. Other upscaling techniques (e.g., blading coating,^[20] slot die, inkjet-printing and spraying) can be further explored to fabricate large-area perovskite optoelectronics.

The concentration of the NiO_x NCs ink is vital for realizing dense and uniform films. Thick films could be deposited by tuning the concentration of NiO_x NC inks, while lower concentrations would lead to pinholes on the as-prepared films. In our previous study, we showed that the flawless NiO_x films cast from an optimal concentration of 2 wt % could realize the best PCE for flexible PSCs with an optimized thickness around 20 nm.^[37] The optimized concentration can be varied upon incorporation of NiO_x NCs into other bilayer or multiple layered HTLs.

More importantly, the superior thermal stability of NiO_x films afford a broad processing temperature window from room temperature up to 150°C without scarifying the hole mobility and inducing detrimental changes in composition. As shown in Figure 4, when the pristine as-deposited NiO_x films were not further heated, contributor peaks of Ni^{2+} state (Ni 2p_{3/2} at 853.6 and O 1s at 529.1 eV for NiO) and Ni^{3+} state (Ni 2p_{3/2} at 855.0 eV and O 1s at 530.8 eV for Ni_2O_3 , and Ni 2p_{3/2} at 856.3 eV and O 1s at 532.1 eV for NiOOH) appeared in the X-ray photoelectron spectroscopy (XPS) spectrum with a ratio of 1.13:1.22:1 ($\text{NiOOH}:\text{Ni}_2\text{O}_3:\text{NiO}$) derived from the calculation of integral area in the Ni 2p spectrum.^[52] And the atomic ratio of Ni and O is around 1:1.14, confirming the non-stoichiometric on the surface of NiO_x films. When elevated the

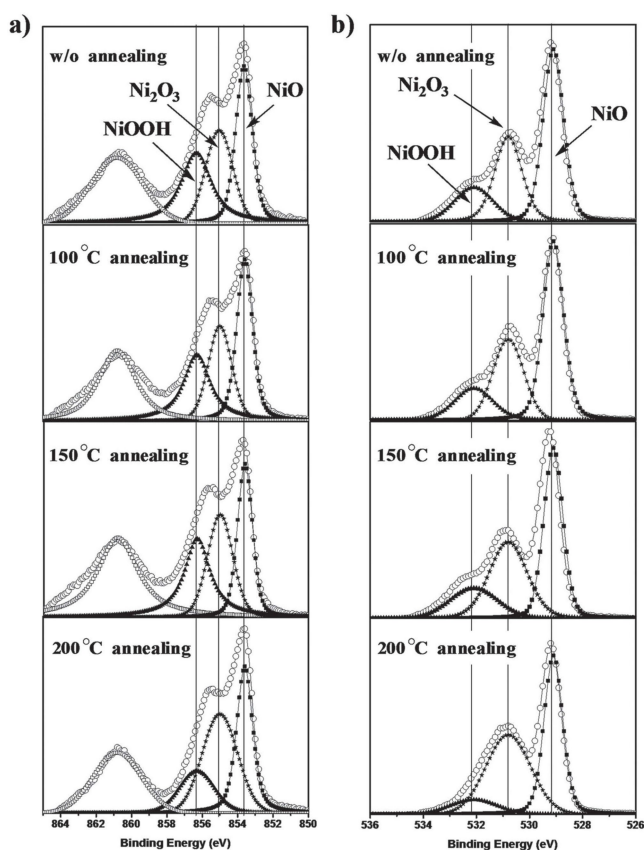


Figure 4. XPS results of NiO_x films under different processing temperatures. a) Ni 2p 3/2, b) O 1s core level peaks. Adapted with permission from Ref. [52].

annealing temperature to 150 °C, there is no obvious changes in the dominant peaks in the XPS results, meaning the composition of NiO_x films is stable and unchanged. While the high annealing temperature of 200 °C would lead to a partial composition changes from NiOOH to Ni₂O₃. The broad processing window would enable the NiO_x NCs easy to process and provide wider applications as HTL in different optoelectronic devices.

4. Surface modification of NiO_x NC films

Although the PCEs of inverted PSCs based on dopant-free NiO_x NCs have reached 20.5 %, [62] closing to 21 %, the high density of defects and energy-level misalignment at the NiO_x/perovskite interface constrain the further improvement of their performance and operational stability. [13,23,45] Such interfacial defects result in poor contact between the NiO_x film and the perovskite layer, which not only influences the perovskite crystallinity and morphology but also causes charge recombination and decreased photovoltage. [13,23] Meanwhile, the NiO_x interface redox reaction with perovskite has been reported to cause challenging issues in device stability. [23,63] The reactions mainly involve the following chemical reaction:



To reduce the density of defects and inhibit the redox reactions at the NiO_x/perovskite interface, modifying the surface properties of the NiO_x NCs film with tailored molecules (e.g., small molecules, polymers, ionic liquids, and organic ammoniums) has been demonstrated to be an effective strategy, as shown in Figure 5. Given the rich hydroxylated groups on the surface of NiO_x NCs, Jen et al. first systematically investigated the separate role of the chemical interaction between the NiO_x NCs film and the perovskite layers by inserting suitable para-substituted benzoic acid self-assembled monolayers (SAMs). [45] SAMs with different dipole moments were used because of the following reasons: i) To serve as a “binder” to improve the adhesion between the NiO_x film and the perovskite layer to facilitate the charge transfer by passivating the inorganic surface trap states; [64] ii) To modify the work function of the NiO_x NCs through their molecular ordering induced by the permanent dipole moments; [65] iii) To change the perovskite crystallinity and morphology through chemical interactions through different terminated functional groups. [66] The Br-BA SAM modifier was found to have a positive effect that largely enhances the PCE to 18.4 % with an increased open-circuit voltage (*V*_{oc}) of 1.11 V, a short-circuit current density (*J*_{sc}) of 21.7 mA cm⁻², and a FF of 76.3 %. In addition, the device stability was improved owing to the minimization of the energy level offset, the reduced surface trap states, the increased perovskite crystallinity, and the enhanced wetting between NiO_x and the perovskite layers, outperforming the control group (PCE of 15.5 %) in terms of PCE and stability. Moreover, we incorporated the Br-BA SAM into the flexible PSCs (F-PSCs) and achieved one of the highest PCE of 16.2 % on the polyethylene terephthalate (PET) substrate with a remarkable power-per-weight of 26.9 W g⁻¹. Recently, Choy et al. synthesized benzoic acid with a -NH₃⁺ substituted tail group, namely, 4-(2-aminoethyl) benzoic acid bromide (ABABr), [27] which chemically reacts with the NiO_x NCs via electrostatic attraction on one hand and forms a strong hydrogen bond via the -NH₃⁺ group with perovskites layers, on the other hand, directly diminishing the redox reaction between the NiO_x and the perovskites layers and passivating the layer surfaces. Additionally, the ABABr interface modification leads to significant improvements in perovskite film morphology, crystallization, and band alignment. More recently, NiO_x NCs were also introduced into the low band gap tin-lead perovskite solar cells (Sn-Pb PSCs) system by Zhou et al. [67] By manipulating the buried NiO_x/perovskite interface with OH-PEAX (4-hydroxyphenethyl ammonium halide, X=Cl⁻, Br⁻, or I⁻) interlayer, the film quality of Sn-Pb based perovskite has been improved, resulting in the reducing of the surface defects and the improving of the energy matching. Benefitting from these, a PCE of 20.53 % is acquired for Sn-Pb PSCs, which is the highest PCE of Sn-Pb PSCs based on NiO_x NCs.

Phosphonic acid-based SAMs have also been employed to modify the surface properties of NiO_x NCs and improve the performance of inverted PSCs. [12,68] For example, Tan

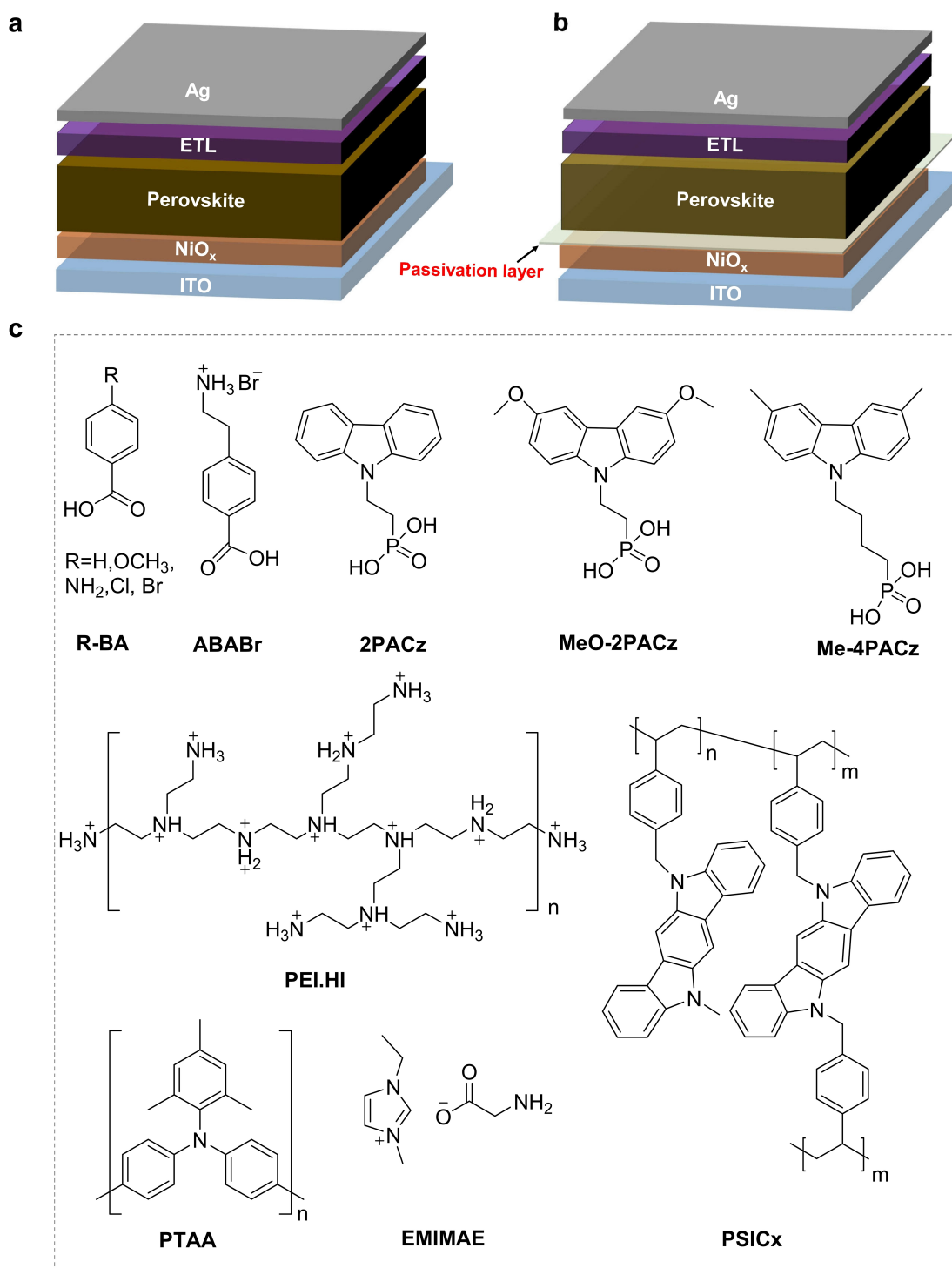


Figure 5. Schematic illustration of inverted PSCs based on a) pristine NiO_x NCs film and b) passivated NiO_x NCs film and c) the representative chemical structure of the passivators.

et al. reported a molecule-bridged hole-selective contact to mitigate interfacial recombination and facilitate hole extraction in inverted PSCs by anchoring a hole-selective SAM on the low temperature-processed NiO_x NCs film. Considering the excellent hole selectivity and effective chemical bonding formation, two types of molecule, namely, 2PACz ([2-(9H-carbazol-9-yl)ethyl] phosphonic acid) and MeO-2PACz

([2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid), were investigated. The 2PACz and MeO-2PACz molecules anchor on the surface of NiO_x NCs via the phosphonic acid group. Meanwhile, the oxygen from the phosphoryl of the 2PACz passivates the defects in the buried interface of the perovskite films via forming the Pb-O chemical bonding, as confirmed by first-principle calculations. The anchoring of

2PACz and MeO-2PACz with different molecular dipole moments (2.0 debye vs. 0.2 debye) can also tune the energy-level alignment between NiO_x and perovskites. Thus, the interfacial non-radiative recombination is suppressed at the interface between the NiO_x and the perovskite, contributing to the improved photovoltaic performance of flexible single-junction PSCs. Furthermore, this strategy can be employed to fabricate flexible all-perovskite tandem solar cells with a certified PCE of 24.4 %, which represents the highest performance among all the types of flexible thin-film solar cells reported to date.

In addition to SAM materials, other small organic molecules and polymers have been investigated to modify the NiO_x /perovskite interface. Their molecular structures are shown in Figure 5c. Min et al. reported a bidentate chelating ligand 2,2'-bipyridine (2,2'-BiPy) to modulate the interfacial properties between NiO_x and the perovskite via its strong chemical interactions with the two layers.^[69] The improved interfacial contact is beneficial to the crystal growth of the perovskite with enhanced crystallinity and reduced trap states, in contrast with the perovskite film on the pristine NiO_x layer. Li et al. reported that the poly-ethylenimine cations (PEI^+) modifier can not only effectively passivate the surface defects of the NiO_x NCs film, but also induce the in situ-generation of PEI-based 2D perovskite interlayers at the NiO_x /MAPbI₃ interface. Such PEI-based 2D perovskite interlayer dramatically mitigates the lattice mismatch between NiO_x and perovskites to suppress the formation of interfacial defects and promote the high-quality crystal nucleation and growth of the above perovskite films.^[70] Meanwhile, the molecular weights of the PEI have a critical role in controlling the nucleation quality of perovskites. When employing a PEI with molecular weight of 10000 (PEI-1000), a high-crystalline perovskite film with large-sized grains and reduced interfacial defects is obtained, and the champion PSC delivers a PCE of 19.23 % with a weak hysteresis effect and improved reproducibility and stability. The polymer PTAA could effectively passivate the surface defects of NiO_x films and enhance hole transport.^[18,19,71] Furthermore, a mesoporous alumina (Al_2O_3) thin layer deposited on the top of the PTAA layer can effectively improve the interface contact and carrier dynamics. Park et al. reported a newly design 5,11-dihydro-indolo[3,2-b]carbazole-based polymeric macromolecule (PSIC_x) that can enhance the interfacial characteristics between the solution-processed NiO_x NCs and perovskite, consequently improving the performance and stability of inverted PSCs.^[72]

Recently, ionic liquids and inorganic salts have also been employed to modify the properties of the NiO_x /perovskite interface. For example, Bi et al. reported a kind of ionic liquid, 1-ethyl-3-methylimidazolium aminoacetate (EMIMAE), which was adopted as an interfacial modifier at the NiO_x /perovskite interface.^[24] The positive and negative charges of the EMIMAE interface layer can interact with PbI_2 and NiO_x , respectively. On this basis, the interfacial layer modifies the NiO_x /perovskite interface and improves the perovskite film quality with high crystallinity and few defects. Additionally, an EMIMAE interface layer can

reduce the interfacial charge accumulation and enhance the hole transport. As a result, the EMIMAE-modified NiO_x based inverted PSCs obtain an optimal PCE of 18.6 % with good operational stability. Choy et al. reported that inorganic salts, such as potassium thiocyanate (KSCN), can not only effectively reduce the defects on the surfaces of NiO_x and perovskite but also result in the improved energy level alignment between NiO_x and perovskite.^[26] Benefiting from these improvements, the charge carrier extraction and transport are significantly promoted. The KSCN treated inverted PSCs based on the NiO_x NCs achieved a PCE of 21.23 %, which is superior to that of the device based on pristine NiO_x (18.69 %).

5. Applications beyond photovoltaics

In addition to their successful applications in PSCs, our dopant-free NiO_x NCs have also been employed as effective HTMs in perovskite-based light-emitting diodes (PeLEDs) and photodetectors (PDs), as illustrated in Figure 6. For instance, Choy et al. reported a high-performance blue PeLEDs using NiO_x NCs as HTL for the first time.^[73] Introducing a thin polymer layer of poly(sodium-4-styrene sulfonate) (PSSNa) on the NiO_x for forming a bilayer HTL structure, simultaneously suppresses the nonradiative recombination through the reduction of the defect states in NiO_x films and improves the morphology of perovskite film by reducing the film roughness and minimizing the pinholes. As a result, the optimized blue PeLEDs exhibit an impressive luminance of 5737 cd m^{-2} , a very low turn-on voltage of 3.31 V, and an external quantum efficiency (EQE) of 1.45 %. Xie et al. reported a simple H_2O treatment of as-prepared NiO_x films, which effectively enhances the brightness and light-emitting efficiency of blue PeLEDs simultaneously by improving the uniformity and morphology of NiO_x films.^[74] The blue PeLEDs employing H_2O -treated NiO_x as the anode interfacial layer show a maximum luminance of 9052 cd m^{-2} and a maximum EQE of 1.80 % (emission peak located at 482 nm). Recently, NiO_x was also employed as HTL in a blue PeLED based on a pure bromide system by Liang et al.^[75] The NiO_x NCs with multiple $-\text{OH}$ groups on their surface are more favorable for the formation of a CsPbBr_3 : Cs_4PbBr_6 blue-emitting perovskite film than the traditional PEDOT:PSS HTL. The NiO_x -based all-inorganic PeLEDs show excellent thermal and spectral stability and a maximum EQE of 1.58 % at an EL wavelength of 491 nm. These dopant-free NiO_x NCs have also been employed to form NiO_x : PbI_2 nanocomposite structures as an effective HTL for perovskite-based PDs.^[76] The nanocomposite structures provide a large electron injection barrier and favorable hole extraction and passivates the surface of the perovskite, leading to suppressed dark current and enhanced photocurrent. By optimizing the NiO_x : PbI_2 nanocomposite structures, a low dark current density of $2 \times 10^{-10} \text{ A cm}^{-2}$ at -200 mV and a large linear dynamic range of 112 dB are achieved. Meanwhile, a high responsivity in the visible spectral range of 450–750 nm, a large measured specific detectivity approaching 10^{13} Jones,

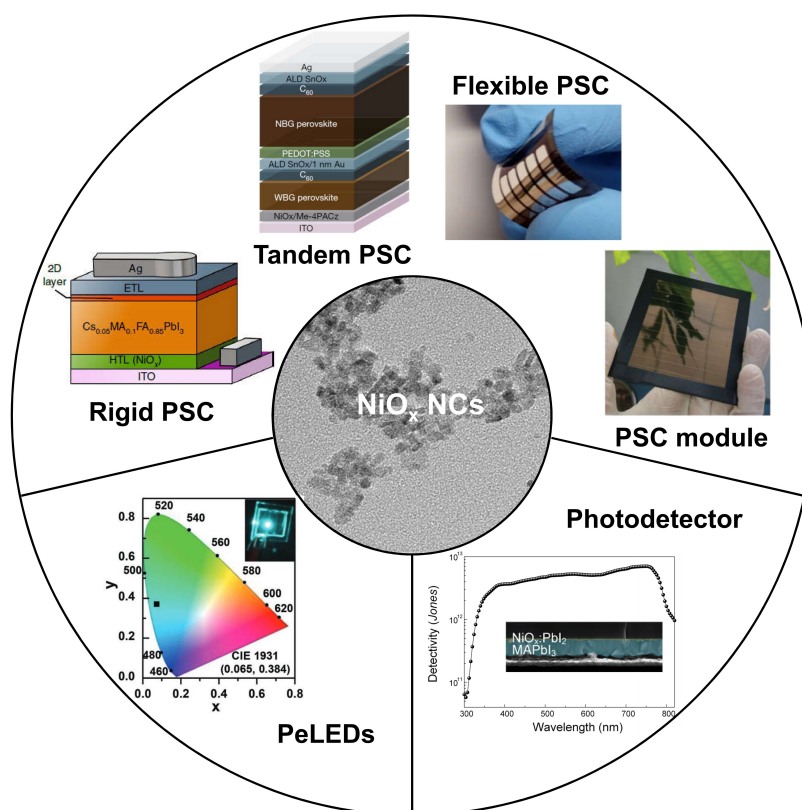


Figure 6. Applications of NiO_x NCs in perovskite-based optoelectronic devices. Adapted with permission from Refs. [12, 25, 37, 43, 74, 77].

and a fast fall time of 168 ns are demonstrated. In summary, these works demonstrate that dopant-free NiO_x NCs are effective HTMs for achieving high-performance perovskite-based optoelectronic devices.

6. Conclusion and Outlook

In this review, we summarize the preparation/modification methods and application prospects of NiO_x NCs, which show a bright future as an efficient and low-cost HTMs for perovskite-based optoelectronic devices. The surface chemical properties of NiO_x NCs are vital for maximizing the device performance and long-term stability.^[77] Exploring different kinds of bases and organic/inorganic ligands in the synthesis process of NiO_x NCs may be an important approach. Meanwhile, more advanced characterizations and comprehensive studies should be conducted to fully understand the formation mechanism of well-dispersed NiO_x NCs and their surface chemistry. The superior dispersion stability and wide temperature processing window of the NiO_x NCs ink also make it promising for wide applications in flexible optoelectronic devices and tandem solar cells fabricated by scalable coating methods, such as blade coating, ink-jet printing, slot-die, and spraying.

Although the modification of the NiO_x /perovskite interface has been demonstrated to be an effective strategy for reducing the interface defect density and manipulating the film quality of perovskite films, revealing the passivation

mechanism is still highly required for guiding the future design of highly effective modification materials. Machine learning may accelerate the development of this process. Not limited in inverted PSCs with a p-i-n structure, there is still a possibility for NiO_x NCs to be applied in the normal n-i-p structure by choosing proper organic solvent to replace the aqueous solvent, which will offer the opportunities to substitute for the unstable organic HTL material, such as spiro-OMeTAD.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Chemical Precipitation Method • Hole Transport Material • Nanocrystal • Nickel Oxide • Perovskite Solar Cell

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