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Progress, Highlights and Perspectives on NiO in Perovskite Photovoltaics

View Article Online
DOI: 10.1039/D0SC02859B

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Abstract

View Article Online
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The power conversion efficiency (PCE) of NiO based perovskite solar cells recently hit a record 22.1% with hybrid organic-inorganic perovskite composition and a PCE above 15% in the full inorganic configuration. Moreover, NiO processing is a mature technology, with different industrially attractive processes demonstrated in the last years. These considerations, along with excellent stabilities reported, clearly point towards NiO as the most efficient inorganic hole selective contact for lead halide perovskite photovoltaics, which is the topic of this review. The NiO optoelectronics is discussed by analysing the different doping mechanisms, with a focus on the case of alkaline and transition metal cation dopants. Doping allows tuning the conductivity and the energy levels of NiO, improving the overall performance and adapting the material to a variety of perovskite compositions. Further, we summarise the main investigation on the NiO / Perovskite interface stability. In fact, the surface of NiO is commonly oxidised, and it is reactive with perovskite under light, thermal and electrical stress. Interface engineering strategies should be considered aiming at the long term stability and the highest efficiency. Finally, we present the main achievement in flexible, fully printed and lead-free perovskite photovoltaics which employ NiO as contact and provide our perspective to accelerate the improvement on these technologies. Overall, we show that an adequately doped and passivated NiO might be the ideal hole selective contact in every possible application of perovskite solar cells.

1. Introduction

Metal halide perovskite solar cells (PSCs) are based on a p-i-n junction, with the perovskite absorber sandwiched between an n-type and p-type semiconductors acting as selective contacts¹⁻³. Steep and tunable light absorption onset, high ambipolar photoconductivity and long photocarriers lifetimes are the key properties of lead halide perovskites behind the rise in power conversion efficiency (PCE) above 25%.⁴ To make the most of perovskite optoelectronics, selective contacts have to extract the photocurrent without introducing ohmic losses, energetic barriers and have to minimise the non-radiative recombination at the interfaces⁵⁻⁸. SnO₂^{9,10}, TiO₂^{11,12} and fullerenes^{13,14} are the best candidates as electron selective layers (ESLs). On the other side, although materials with excellent performances in term of efficiency and stability have been developed¹⁵⁻¹⁷, Spiro-OMeTAD and PTAA remain the standard hole selective contacts (HSLs).

Spiro-OMeTAD films have very low conductivity (below 10⁻⁷ Scm⁻¹), and ingenious doping strategies have been developed to overcome this limitation and minimise ohmic losses. LiTFSI is employed to catalyse the Spiro-OMeTAD oxidation from the atmospheric oxygen, resulting in a 100-



fold increase in conductivity¹⁸. Alternatively, protic ionic liquids¹⁹ and molecules with high electron affinity can act as dopant, as in the case of F4TCNQ doped PTAA²⁰. Besides the HSL conductivity, the interplay between charge transfer and charge recombination at the perovskite / contact interface is mostly affected by interface energetics and defect density. The highest occupied molecular orbital (HOMO) of PTAA (-5.2 eV) and Spiro-OMeTAD (-5.1 eV) lies slightly above the valence band (VB) of CH₃NH₃PbI₃²¹. This induces a driving force for the hole extraction and assures a high built-in potential, which slows down the non-radiative recombination⁵. Additionally, a passivation layer⁷ or careful molecular tailoring^{22,23} can be exploited to minimise the interface recombination.

NiO has a VB within -5.0 eV and -5.4 eV which leads to a good energy alignment with common lead halide perovskites. Its main drawback is the relatively low open circuit voltage (V_{oc}) of devices, due to the high interface recombination. Nonetheless, NiO is the most promising inorganic p-type hole selective contact for perovskite photovoltaics, showing the highest efficiencies and the better reproducibility among different research groups when compared to other suitable inorganic p-type semiconductors^{24–26}. Compared to Spiro-OMeTAD and PTAA and other organic hole selective contacts, NiO is orders of magnitude less expensive²⁷ and holds great promises in term PSCs' stability. The solar cells' failure commonly follows the intermixing and reaction between perovskite and adjacent layers, especially metal electrodes. Molecular or polymeric selective contacts hardly prevent this interdiffusion^{28–32}. In addition to that, dopants such as LiTFSI and tert-butyl pyridine can diffuse and react with the perovskite and contacts^{33–35}, further degrading the device performances. A uniform NiO layer ideally insulates the perovskite film from the electrode, thus preserving the structural integrity of the device.

In this review, we highlight the main advancement concerning the implementation of NiO in perovskite solar cells, a successful story yielding PCE over 22% and operational stabilities of over 1000h. While not aiming at a complete covering of the latest research on NiO (for which we recommend the references^{25,26}), we focus on the material chemistry behind the NiO working principles to understand the role of NiO defects, doping density and surface chemistry on the perovskite solar cells behaviour. We discuss industrially attractive NiO implementation by considering scale-up compatible processes and flexible photovoltaics. Finally, we summarise the latest findings and provide guidelines for future developments of printable and lead-free perovskite solar cells, the next breakthroughs in perovskite photovoltaics.

2. NiO in Perovskite Solar Cells



Nickel oxide is the most attracting inorganic p-type semiconductor to act as hole selective contact in perovskite photovoltaics, with the research community being increasingly interested in that as shown in figure 1a, where the “publication rate” (i.e. number of papers per month) increases by a factor 20 in about five years. NiO is usually implemented in the inverted (p-i-n) architecture, with the perovskite film grown on top of NiO from which light shines through the device. In this configuration, efficiencies above 20% have been demonstrated. Moreover, tremendous efforts resulted in a vast range of alternative NiO deposition techniques, including industrially attractive routes. Some of these techniques are, in principle, compatible with processing NiO on top of the perovskite film, which would enable full-inorganic n-i-p perovskite solar cells, an ideal solution to combine the highest efficiency and stability.

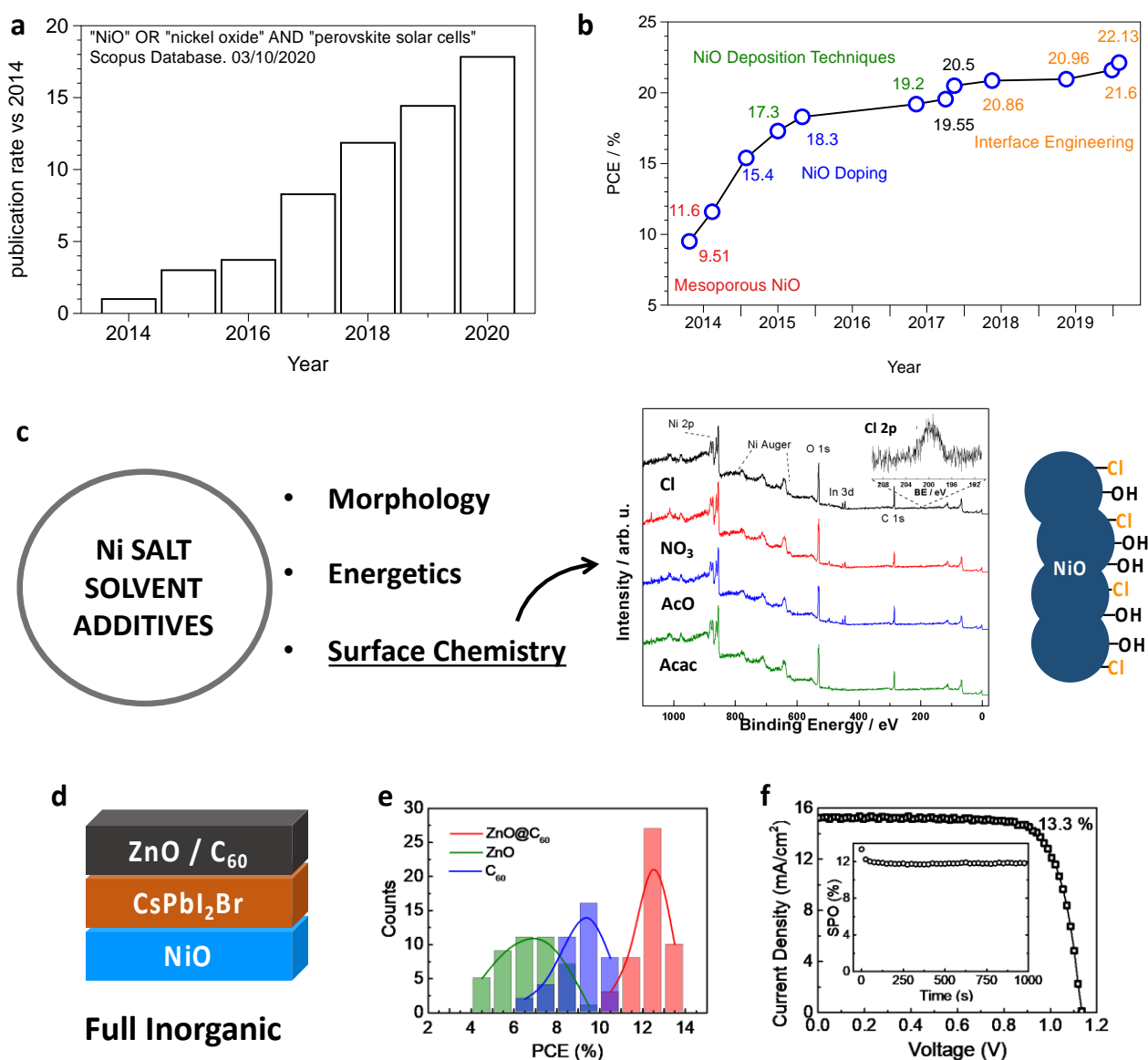


Figure 1. a) Publication rate evaluated as the number of papers per month as calculated by the Scopus database for the “NiO” and “Perovskite solar cells” keywords. b) Record PCE chart for p-i-



n perovskite solar cells employing NiO as hole selective layer. References ^{36–46} The key approaches leading to record efficiency are indicated. **c)** Scheme linking the NiO precursor formulation to critical properties of the final NiO films. The effect of the Ni precursor on the surface chemistry is highlighted by XPS investigation (as described in ref⁴⁷) on NiO films processed from NiCl₂, Ni(NO₃)₂, Ni(AcO)₂ and Ni(acac)₂ showing that chloride remains bound to the surface **d)** Example of full inorganic (perovskite and selective contacts) PSC configuration **e)** Dependence on the electron selective layer of the PCE of full inorganic NiO/CsPbI₂Br PSCs. **f)** Best cell from figure 1d with the complete inorganic configuration NiO/CsPbI₂Br/ZnO@C₆₀. Figures **e)** and **f)** are reprinted with permission from ref 48. Copyright 2018 American Chemical Society.

2.1 P-i-n Perovskite Solar Cells

The power conversion efficiency justifies the prominent role of NiO as inorganic hole selective contact, with several demonstrations above 20% in the last two years and a (not certified) record of 22.13%³⁸. In figure 1b we show the record chart for single-junction perovskite solar cells employing NiO as hole selective contact, which also highlights the most critical approaches developed to effectively implement NiO into perovskite solar cells, which will be discussed throughout this review article. The most efficient NiO based PSC is the planar p-i-n architecture, where a ~20nm thin NiO layer is deposited employing sol-gel chemistry principles or from a NiO nanoparticles ink. One of the most robust protocol consists of the spin-coating of a nickel acetate solution in 2-methoxyethanol with monoethanolamine as stabilising / complexing additive⁴⁹. Alternatively, by adding acetylacetonate to a nickel nitrate solution a combustion reaction allows to reduce the annealing temperature from above 300°C to 250°C⁵⁰, and even to 150°C when copper as a dopant is included⁵¹. In our lab, we achieved 20% of PCE (unpublished results) by employing a nickel chloride solution with nitric acid as additive. Notably, our procedure spontaneously leads to a chloride capped NiO film, as shown in figure 1c, which is particularly interesting since the chloride functionalisation was found beneficial in term of interface recombination for TiO₂⁵² and SnO₂⁵³. Finally, the spin-coating of NiO nanoparticles ink brings the main advantage of the abatement of the post-deposition annealing^{54,55}. We remark that the selection of the most performing “NiO recipe” is not an easy task. In fact, a meaningful comparison between the different procedures will be possible only with a general improvement on the description of the experimental methods⁵⁶ (which will also positively impact figure 1b). As an example, the relative humidity is difficult to control and almost never reported, but it has a strong influence on the formation of metal oxides, where water may act as a reagent.



The highest efficiency NiO-based PSCs exploit formamidinium based mixed-cation mixed-halide composition, closely following the general trend in perovskite photovoltaics. However, NiO might be particularly well suited also for the fabrication of fully inorganic perovskite solar cells. Avoiding the organic A-site cation improves the thermal⁵⁷ and environmental^{58,59} stability of APbX₃ perovskites. Further, the introduction of inorganic semiconductors at both contacts inherently encapsulates the perovskite. Typically, a CsPbI₂Br stoichiometry (or even richer in bromide⁵⁷) is adopted to overcome the phase instability of CsPbI₃, stable at room temperature in the non-photoactive δ -CsPbI₃ (even if it is possible to substantially extend the metastability in Cs-rich condition⁶⁰ or by tuning the strain of the thin film⁶¹). The adoption of the composite ZnO@C₆₀ electron selective layer in NiO/CsPbI₂Br based PSCs was found crucial to achieve an efficiency above 13% in full inorganic perovskite solar cells (figure 1c and 1d),⁴⁸ lately improved by doping C₆₀ with LiClO₄ and tris(pentafluorophenyl)borane (TPFPB) to attain a remarkable 15% PCE⁶². Further improvement will likely be achieved by treating the NiO surface, as shown by Yang *et al.* to boost the efficiency of NiO/CsPbBr₂I based PSCs from 6.3% to 9.5%⁶³.

2.2 Beyond Spin-Coating

The up-scaling process became crucial for the exploitation of perovskite solar cell technology at industrial level. Recently, research institutes and R&D companies spent considerable efforts to speed up the manufacturing process of perovskite solar modules at high technology readiness level (TRL). In this aim, the research on cost-effective, scalable, high throughput deposition techniques needs to be addressed as a hot topic for the future development of PSC photovoltaic technology. Considering the whole manufacturing process, necessary actions have to be considered concerning the scalable deposition of the entire stack forming the PSC devices. On this topic, the uniform and scalable deposition of the hole transport layers play an essential role for both n-i-p and p-i-n device architectures. On the other hand, processing temperature and operational stability of HSLs have to take in account too. NiO offers considerable opportunities to match all these requirements.

The NiO layers have been deposited by well-established industrial relevant physical and chemical vapour deposition techniques. Techniques like sputtering^{64,65}, pulsed laser deposition (PLD)⁶⁶, thermal⁶⁷ and electron-beam evaporation⁶⁸, chemical vapour deposition (CVD) and atomic layer deposition (ALD)⁶⁹ have been introduced for the manufacturing of NiO layer of highly efficient inverted p-i-n perovskite solar cells, approaching 20% in PCE⁶⁸. Whether these techniques could represent the convenient industrial process for NiO deposition would depend, besides the quality of the NiO layer, on costs and throughput. Ideally, the use of vacuum-free printing techniques based on



solution processing might fit those requirements. Methods like chemical bath deposition (CBD)⁷⁰, electrodeposition^{42,71}, spray pyrolysis^{72,73}, blade coating and screen-printing are, therefore, highly attractive. At the same time, it could be convenient to adopt processing routes which can be straightforwardly implemented into already operative industrial line. With this in mind, an available and cost-effective solution could consist in the deposition of NiO film during the manufacturing process of transparent conductive oxides (TCO). The most used TCOs for PSC technology are indium tin oxide (ITO) and fluorine-doped tin oxide (FTO). The ITO coating is generally deposited by sputtering and commercially available on both rigid glass and flexible plastic substrates. FTO is made by spray pyrolysis deposition (SPD) at high processing temperature limiting its use on glass substrate only. Sputtering and SPD are both suitable techniques for high-quality NiO film, which makes the integration of the deposition in the manufacturing process of TCO as the most advantageous option. Sequential manufacturing of the TCO and the NiO HSL in the same production line can guarantee better reproducibility and high throughput process. Different is the case for tandem photovoltaics, where the PSC acts as a wide-bandgap device in combination with silicon or CIGS. Mechanically stacking the PCS on top of the silicon solar cell, as shown by Lamanna *et al.*⁷⁴, would directly enable every NiO deposition demonstrated in the literature. Nonetheless, aiming at processing the PSC on top of textured silicon solar cell in a monolithic tandem device, sputtering might be the ideal technique for the deposition of a 15-20 nm thick conformal NiO layer, as demonstrated by Hou *et al.* who certified a PCE of 25.7%⁷⁵. Alternatively, Jost *et al.* employed ALD to deposit NiO on top of rough CIGSe solar cell, and achieved a 21.6% PCE when introducing a thin PTAA passivation layer to improve Voc and fill factor (FF) of the perovskite device⁷⁶.

2.3 N-i-p Perovskite Solar Cells

Specular to the approach of full inorganic p-i-n perovskite solar cells, the introduction of NiO as hole selective contact in n-i-p architecture is one of the most promising routes to stabilise perovskite photovoltaics. Excellent demonstrations are the CuSCN/rGO hole selective contact developed by Arora *et al.*⁷⁷, and the 16 months of shelf-life stability by employing NiO and TiO₂ as contacts in p-i-n architecture demonstrated by Zhao *et al.*⁷⁸

Despite the great promises, few demonstrations of NiO in n-i-p PSCs have been reported to date, all exploiting inks of NiO nanoparticles (NPs) based on solvents orthogonal to perovskite due to the high temperature needed for the other deposition of NiO. The standard approach is to produce functionalised NiO nanoparticles, capped with an organic specie which allow the solubility in aromatic or alcoholic solvents.^{79–82} The PCE is within 12% and 9%, due to the negative impact of the



organic shell on the conductivity of the NiO layers and on the hole transfer from the perovskite. In fact, Liu *et al.* observed an increase in PCE in the p-i-n architecture after removing part of the ligands with an UV-ozone treatment⁸¹, a procedure not compatible for n-i-p devices. Another reason for the relatively poor performances might be the quality of the NiO film, in term of NPs packing and electrical contact with the perovskite. To this aim, a finer tuning of deposition technique, NPs size and size dispersity might enable more efficient contacts. An alternative is to fill the NiO NPs film with an organic or polymeric hole selective contact, as in the case of NiO | Spiro-OMeTAD bi-layer shown by Li *et al.*⁸³, who demonstrated a 21.6% efficiency. Moreover, the authors suggest that NiO might act as a protecting layer, slowing down the diffusion of Spiro-OMeTAD dopants into the perovskite layer, thus stabilising the device.

2.4 Safety Hazards

The use of NiO presents some safety concerns due to its toxicity. Nickel itself is suspected of causing cancer, can cause an allergic reaction and may cause damage to organs. The NIOSH suggests a recommended exposure limit of 0.015 mg m⁻³ for continuous exposure of 8 hours.⁸⁴ Nickel oxide shows similar hazards, however, the potential exposure when deposited as a well-bonded thin film can be considered very limited. The main risk occurs in the deposition phase, raising safety concerns for the operators. In a sol-gel synthesis, each nickel precursor has specific toxicity: while nickel acetate is less harmful than nickel, nickel nitrate and nickel chloride present some additional risks.²⁷ Commonly used solvents like 2-methoxy ethanol, acetylacetone, and ethylene glycol are also increasing the risk if the operator is exposed to the sol-gel ink or its fumes.

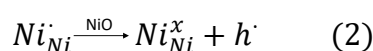
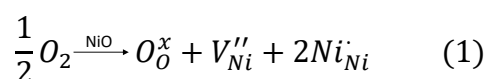
Nevertheless, with the appropriate use of personal protective equipment (PPE) as well as a confined deposition environment, it is possible to minimise risks. Other solvents as alcohols or water can lower the requirements for ventilation, and their use should be encouraged. When nanoparticles are used, their smaller size and their airborne nature represent a significant increase in the risks. Recent studies suggest that the exposure limit should be 10 times lower than bulk nickel oxide,⁸⁵ and it is essential to have strict control on the handling dry nanopowders. For the same reason is vital to ensure good adhesion with the substrate (especially on a flexible substrate in a roll-to-roll production) to avoid releasing airborne particles. When NiO is deposited by sputtering or e-beam evaporation, the film is usually well bonded to the substrate and the risks is mostly limited to the periodic cleaning of the chamber or due to deposition of flakes from the target on samples. We want to emphasise that it is essential to develop appropriate safety procedures when handling this material, both during a research and development phase as well as in the eventual industrialisation phase. We also believe that with



good control of the thin film deposition procedure, it is possible to use Ni and NiO without risks, as the material is already widely used in the industry.

3. Doping of NiO

NiO is an insulator in its stoichiometric form, with its p-type conductivity arising from the self-doping mechanism due to the Ni²⁺ vacancy (V''_{Ni} , the thermodynamically most abundant point defect). In Kröger-Vink notation the self-doping mechanism can be written using equations 1 and 2:



The twofold negative charge of the nickel vacancy is compensated by the stabilisation of the Ni³⁺ oxidation state (Ni_{Ni}^{\cdot}), which act as an acceptor shallow level. This picture serves as basis to understand the NiO doping, which could proceed through the substitutional replacement of Ni²⁺ with a cation with a lower oxidation state (e.g. Li⁺ or Ag⁺) or by modifying the oxidation state (non-stoichiometry) of the film.⁸⁶ Moreover, dopants can influence the optoelectronics of NiO by modifying its work function or ionisation potential, as in the case of alkaline-earth cations doping.^{64,87} Before discussing in detail the doping mechanisms from alkaline and transition metal cations it is important to remark that non-metal and molecular doping is also suitable to improve the NiO performances. Zhou *et al.*⁸⁸ reported the improving of the hole extraction from perovskite by including nitrogen (through guanidinium nitrate) in the NiO. Additionally, some of the highest performances (>20% of PCE) have been demonstrated by implementing molecular doping either confined at the surface⁴⁵ or throughout the whole NiO layer (in films deposited from NiO nanoparticles ink)³⁸. The molecules employed (such as F6TCNNQ) extract electrons from NiO in virtue of their high electron affinity (above 5.3eV) and establish a strong interaction with the NiO surface, which assures the stability of the molecular doping after the processing of perovskite. Notably, the surface doping was demonstrated by employing electrostatic force microscopy and distinguished from the mechanism of surface passivation.⁴⁵



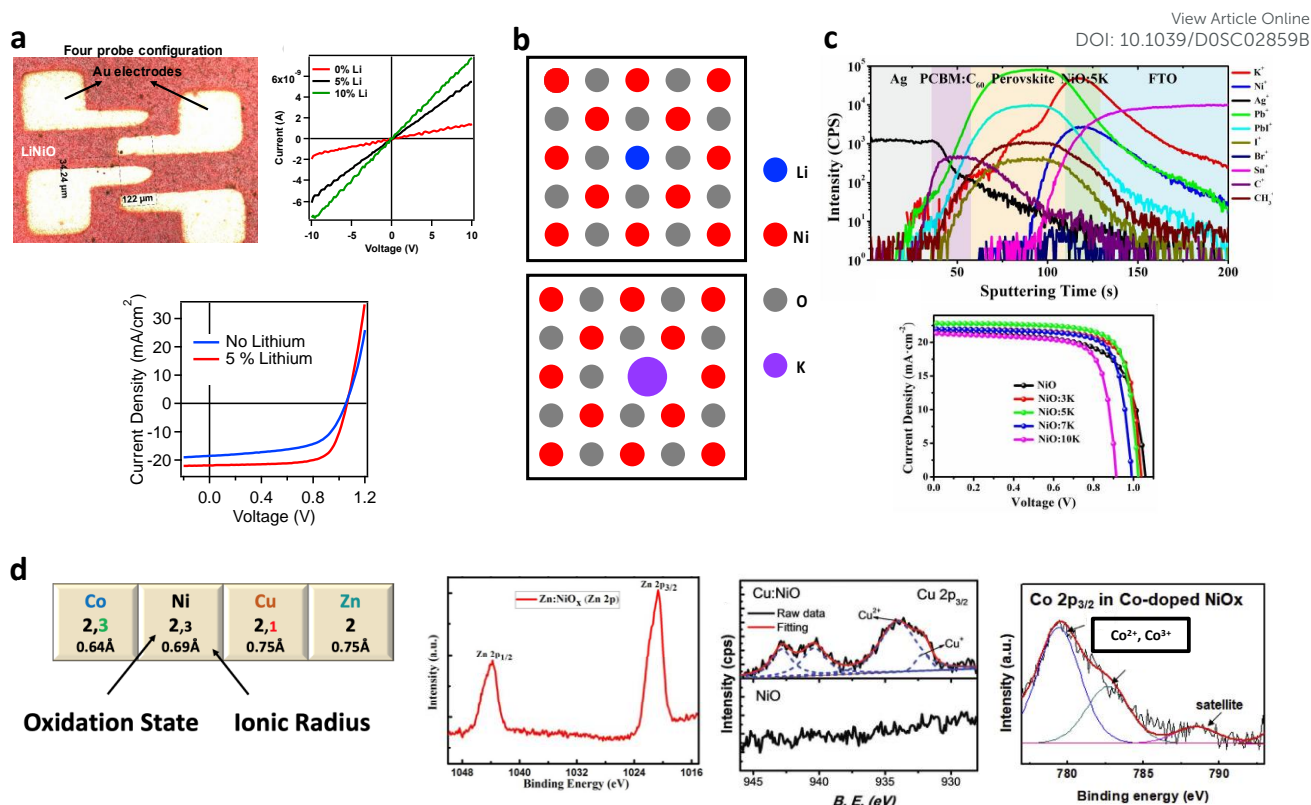


Figure 2 a) Configuration for measuring the conductivity of Li:NiO with the improvement of J_{sc} and FF in the perovskite solar cell, Reproduced with permission from ref 89. Copyright 2018 John Wiley and Sons. b) Scheme for the substitutional replacement of Ni^{2+} with small Li^+ and large K^+ c)

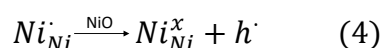
Depth profiling of a perovskite solar cells showing that K^+ is also found in the perovskite after diffusion from the K:NiO. Below are shown the JV curve at different doping level for K:NiO.

Reproduced with permission from ref 90. Copyright 2019 Royal Society of Chemistry. d) Most abundant oxidation state with the most common ionic radius for Ni and appropriate transition metal dopants. XPS spectra for doped NiO films are reported to highlight the mixture of oxidation states in the case of Cu and Co. Reproduced with permission from ref 91. Copyright 2018 American Chemical Society. Reproduced with permission from ref 92. Copyright 2018 John Wiley and Sons.

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3.1 Alkali Cation Doping

In Kröger-Vink notation, considering Li^+ , the alkaline cation doping of NiO via Ni^{2+} substitutional replacement⁹⁴ can be rationalised with equations 3 and 4:



The negative charge of Li'_{Ni} is compensated by the Ni^{3+} acceptor level. A significant increase in FF and Jsc of PSCs follows the enhanced conductivity of NiO upon lithium doping, as shown in figure 2a and reported by many authors^{66,89,95,96}. Moving down through the alkaline group, the energetic cost for Ni^{2+} substitutional replacement increases due to ionic radius mismatch (e.g. $Ni^{2+}=0.69\text{\AA}$, $Li^+=0.76\text{\AA}$, $Cs^+=1.67\text{\AA}$), and different doping mechanisms operate. Interestingly, a combined XAFS and theoretical investigation on molecular beam epitaxy (MBE) deposited K-doped NiO films suggested that potassium tends to clusters and floats to the NiO surface. At the same time the formation in traces of K'_{Ni} is promoted by additional adjacent oxygen and/or nickel vacancy in order to compensate for the large radius of K^{+97} , as sketched in figure 2b. This is coherent with the work from Yin *et al.* reporting an increase in PCE from 15.77% to 18.05% by doping K^+ into NiO.⁹⁰ In fact, along with an increased conductivity for the K:NiO hole selective layer, a sizable amount of potassium was found to diffuse out of the NiO crystallites and inside the perovskite film (figure 2c). Similarly, in our work, we found little if any evidence for Na^+ inclusion into the NiO lattice. However, the sodium segregation out of the NiO crystallites was beneficial in term of traps passivation⁹⁸. The segregation of alkaline cations at the NiO surface might improve the device performances thanks to the beneficial interaction with perovskite, as observed for accidentally included sodium⁹⁹ and deliberately included potassium^{100,101}. It must be considered that the spatial distribution of the dopants might vary with time, thus modifying the performances of the solar cell. In particular, the small size of lithium makes this cation mobile in perovskite³⁵ and NiO¹⁰². Therefore, a sizeable lithium drift might be expected when the photovoltage develops at the NiO/Perovskite interface. Larger dopants could be exempt from this criticality. With this in mind, it is particularly interesting the increase in conductivity for Cs-doped NiO, which in synergy with an increased work function (from 4.89 eV to 5.11 eV) leads to the rise of the PCE from 16% to above 19%.¹⁰³ Notably, Kim *et al* observed a decrease in the metallic Ni content by introducing Cs^+ in the precursor solution¹⁰⁴, unveiling an unpredictable role in enhancing the phase purity of solution-processed NiO for the alkaline additive.

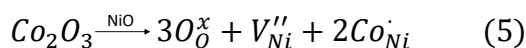
3.2 Transition Metal Cation Doping

Silver is the only transition metal (TM) cation employed as a dopant for NiO stable in the +1 oxidation state, thus bringing a doping mechanism similar to lithium¹⁰⁵. Interestingly, a synergy between lithium and silver in tailoring the optoelectronic properties of NiO has been reported by Xia *et al.*⁹⁶, who demonstrated a 19.24% efficient PSC.

To understand the doping from the other TM cations, we have to consider their respective stable oxidation states, as shown in figure 2d. Zn^{2+} is isovalent with Ni^{2+} , and the ionic radius mismatch is



within 10%, both conditions promoting the substitutional replacement. The increase in J_{sc} and FF behind the PCE jump from ~18% to 19.6% reported by Wan *et al.*⁹¹ when introducing a 5% of Zn^{2+} was explained by means DFT simulation. The calculation showed that the replacement of Ni^{2+} with Zn^{2+} reduces the nickel vacancy formation energy. Notably, a similar concept has been proposed by Kim *et al.*³⁹ to explain the doping mechanism of Cu, whose most abundant oxidation state is Cu^{2+} . However, Chen *et al.*⁹² revealed the presence of a minor fraction of Cu^+ into NiO using XPS. The combined effects of increasing the number of nickel vacancies from Cu^{2+} along with lithium-type doping from Cu^+ might explain the effectiveness of Cu doped NiO, also exploited in copper doped NiO nanoparticles in planar¹⁰⁶ and mesoscopic configuration.⁴³ When doped into NiO, cobalt exhibits a mixture of Co^{2+} and Co^{3+} .⁹³ Natu *et al.*¹⁰⁷, following the work of Radwanski *et al.*¹⁰⁸, proposed that Co^{2+} enhances the acceptor state density in NiO being able to accept an extra electron in its t_{2g} levels. The role of Co^{3+} is not clear. As a hypothesis, Co^{3+} might replace Ni^{3+} in the equilibria involving the nickel vacancies, via the following equation:



This is somehow similar to the mechanism proposed to explain the increase of p-type conductivity in Al^{3+} doped NiO.¹⁰⁹ Besides several demonstrations of successful cobalt doping of NiO to increase the performances of PSCs,^{95,110} a particularly exciting work by Hou *et al.*¹¹¹, reported a mixed amorphous Ni-Co oxide (with Ni:Co 1:1, even though the formation of $NiCo_2O_4$ cannot be discarded entirely), demonstrated as efficient contact for 20% perovskite solar cells, paving the way for a broad family of mixed oxides as hole selective contacts.

4. NiO / Perovskite Interface

The control of the NiO/Perovskite increases the degree of complexity for making highly efficient NiO-based perovskite solar cells. The chemistry of the NiO surface can be rather complex as one can notice from the several Ni peaks in XPS spectra.^{112,113} Different oxidation states (Ni^{3+} , Ni^{2+}) due to defects or to the presence of hydrates ($NiOOH$) and secondary phases (Ni_2O_3 or α/β - $Ni(OH)_2$) are standard for low-temperature synthesis^{114–117}. These defects modify the energy levels, the carrier concentration and mobility of the material, influencing the charge extraction, recombination rates, and the stability at the NiO/perovskite interface. The uneven surface also affects the growth of the perovskite layer, which amplifies the effect of the surface chemistry, requiring additional optimisation and complicating the comparison among different reports in the literature. The growth of the perovskite layer on any metal oxide often causes the decomposition of the organic cation at the interface, influencing the electronic properties and potentially increasing the recombination rates.^{118–}



¹²⁰ In the specific case of NiO, this behaviour is affected by the defects present at the interface. As an example, the same perovskite deposition can lead to the formation of PbI₂ when a sputtered NiO is used while this phenomenon does not occur on solution-processed NiO.¹²¹ This excess is caused by the degradation of methylammonium at the interface with the NiO, and to counteract this effect the perovskite would require either a post-treatment with additional cations or the use of an A-site cation excess in ink. Alternative deposition techniques as the hot-casting method seem less prone to give rise to defect at the interface.⁸⁹ These phenomena show that improvement in the energy alignment and reduction on the defect in the perovskite growth can be achieved by modifying the synthesis of NiO but also by tailoring the perovskite deposition.

4.1 Charge dynamics at NiO / Perovskite Interface

From a fundamental point of view, the NiO interface can extract holes in times down to the sub-picosecond scale, and the wide bandgap allows slowing down the recombination to the order of hundreds of picoseconds.¹²² For these reasons, the interface is not considered a limiting factor in the hole extraction when compared to PEDOT.¹²³ However, the NiO interface can have a large number of defects. Defect engineering has been widely applied to improve the performance of NiO based devices, either by tuning the concentration of Ni³⁺ or by inducing the formation of additional NiOOH.^{124–127} Increasing Ni³⁺ concentration can improve conductivity and charge transfer, but at the same time, it causes non-negligible parasitic absorption.^{125,128} The proper use of NiOOH also appear complex due to the very different energetic levels at the different crystalline surfaces.¹²⁹ Extrinsic doping seems like a more promising approach because it allows tuning of conductivity, work function and bandgap without the optical losses due to Ni³⁺. The presence of Ni³⁺ sites at the interface is also not required for the extraction of charges since there is evidence that hole is transferred to the Ni²⁺ sites.¹³⁰

4.2 NiO / Perovskite Interface Stability

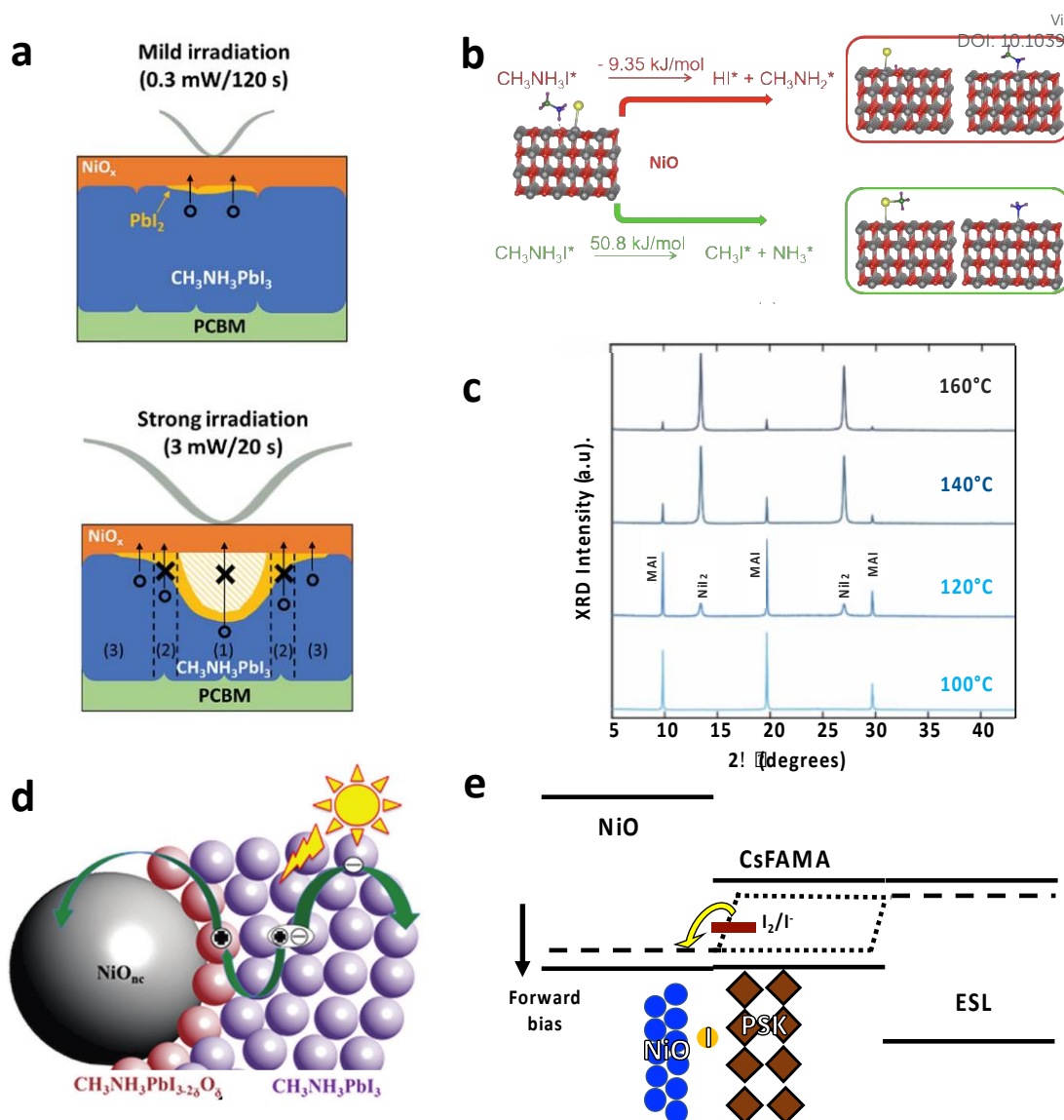


Figure 3 a) The formation of PbI₂ at the NiO/CH₃NH₃PbI₃ upon light irradiation and the effect on charge transport. Readapted with permission from ref 131. Copyright 2018 Royal Society of Chemistry. b) Reaction enthalpies for the decomposition of methylammonium iodide on NiO surface, Reproduced with permission from ref 132. Copyright 2020 American Chemical Society. c) XRD spectra of NiO exposed to methylammonium iodide solution at increasing temperature showing the formation of NiI₂, Readapted with permission from ref 133. Copyright 2019 American Chemical Society. d) Scheme for the formation of an oxygen-containing perovskite at the NiO interface, Reproduced with permission from ref 134. Copyright 2016 John Wiley and Sons. e) Scheme for redox chemistry at the NiO/Perovskite interface. Readapted with permission from ref 124. Copyright 2019 John Wiley and Sons.

Perovskite solar cells with NiO are usually considered to be very stable, with several reports that show high stability under light (with UV) and thermal stresses that would allow passing several IEC



tests.^{68,135–137} The main reason is the structural stability of the NiO layer, preventing the contact of perovskite with the electrodes. Nevertheless, the NiO/perovskite interface can show some specific degradation mechanism that should be prevented to fabricate stable devices. In particular, the formation of NiI₂ has been detected upon thermal degradation of NiO/Perovskite interface.^{132,133} The process is triggered by the large negative enthalpy of NiO reaction with HI, arising from MAI (figure 3b).¹³² Under electrical bias, the interaction between NiO and iodide can result in redox reactions, that can explain the JV hysteresis and impact the interface stability (figure 3e).¹²⁴ Light soaking might be beneficial improving the perovskite crystallinity¹³⁸ or either induce the interface degradation to NiI₂ (figure 3c)¹³⁹ or PbI₂ (figure 3a)¹³¹. The formation of oxygen-containing perovskite interphase (CH₃NH₃PbI_{3-2x}O_x, figure 3d) has been proposed as well, which can induce interfacial p-doping, but also open a new pathway towards degradation.¹³⁴ It is worth noting that the reports on light soaking test beyond 1000 hours employ inks with a stoichiometric composition of cation and anion, so preventing the formation of PbI₂ could help to improve the durability of the interface.¹³⁵ Other solutions are the use of hybrid interlayers as magnesium acetate or ionic liquid as 1-butyl-3-methylimidazolium tetrafluoroborate to enhance the interface among NiO and perovskite, with enhancements in both performance and stability.^{124,135} In particular, the former can improve the NiO interface electrical stability while the latter is useful to prevent the segregation of halides.

4.3 NiO Functionalisation

Surface treatments as oxygen plasma or UV/O₃ can be a valid approach to modify the surface of a metal oxide. Still, the results in perovskite solar cells are not consolidated and are, probably, strongly dependent on the starting condition (the type of NiO and the perovskite synthesis).^{124,140} The functionalisation of the NiO surface appears more suitable to achieve reproducible improvements and to be less sensitive to the synthesis of NiO. A double layer is also often used in efficient OLED to differentiate the function of selective transport and charge injection, and a similar approach could be used here for hole extraction and electron blocking. Functionalisation of NiO can be achieved with inorganic,⁴⁶ hybrid¹²⁴ or organic compounds.^{45,118,120,141–145} We believe that this approach will be key to maximise the performance of PSC with NiO. For instance, the introduction of a thin PTAA coating on NiO reduces the interface recombination¹²⁰ and similar effect has been observed with alternative polymers¹⁴⁶ or by treating the NiO surface with different alkali halides: KCl⁴⁶, NaCl⁹⁸ or CsBr¹⁴⁷. Another possibility is to graft self assembled monolayers (SAMs) on NiO surface, by bonding the through amines¹¹⁸, carboxylates¹⁴² and thiols¹⁴⁸ with phosphonic acid also potentially effective. An organic interlayer, also exploiting the versatility due to the tunable molecular structure (especially in



the case of SAMs), could tackle different issues as control of the surface chemistry, defect-free growth of perovskite, the reduction of mechanical stress, and formation of covalent bonding. In this way, it will be possible to stabilise the interface, promote an appropriate growth of the perovskite and improve the V_{OC} of p-i-n solar cells to achieve efficiencies in par with n-i-p devices.

5. Broad Application of NiO in Perovskite Photovoltaics

Perovskite photovoltaics is attractive for a broad range of application. Low-temperature processing is compatible with flexible substrates. In combination with the excellent performances under indoor lighting¹⁴⁹, this could have a significant impact on IoT (Internet of Things). Additionally, the low costs can be further abated by printing the counter electrode. Especially when considering consumer electronics and wearables the chance to go lead-free is of paramount importance^{150,151}.

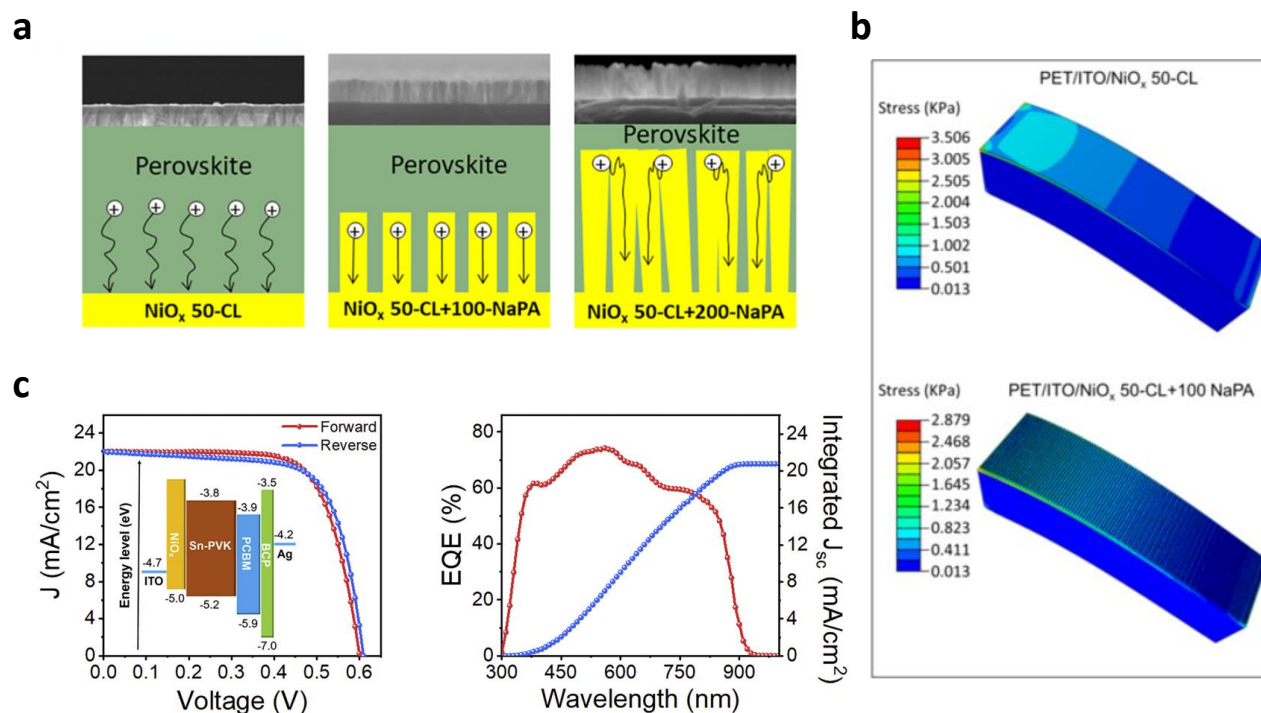


Figure 4 a) Morphology and hole transfer mechanism for the NiO nanopillar array as discussed in ref ¹⁵². b) Finite element simulation showing the lower stress for the nanopillar array NiO layer, from ref ¹⁵². Figures a) and b) Reproduced with permission from ref ¹⁵². Copyright 2019 American Chemical Society. c) Device architecture, JV curve and IPCE for a 10% efficient lead-free perovskite solar cell employing NiO as hole selective contact. Reproduced with permission from ref ¹⁵³. Copyright 2018 Elsevier.

5.1 Flexible Perovskite Solar Cells



Plastic substrates limit the processing temperature to below 150°C ¹⁵⁴. This makes the NiO nanoparticles ink route the sole compatible solution process^{54,155}. Doping NiO nanoparticles in flexible PSCs boost the efficiency from around 13% (undoped NiO)^{54,155} to above 16% with Cu:NiO¹⁰⁶ and to 14.5% with Fe:NiO¹⁵⁶. A remarkable increase to 20% in PCE has been achieved with the molecular dopant F2HCNQ³⁸. Excellent operational stabilities (>90% PCE after 500h of MPPT) have been demonstrated combining a PCBM/ZnO electron selective contact and the NiO NPs layer¹⁵⁷. Minor loss of efficiency after 1000 bending cycles at a radius of 5-8mm was also demonstrated^{38,106,157}. 2-D materials might be particularly well suited for flexible electronics, thanks to their electrical and mechanical properties¹⁵⁸. In particular, graphene quantum dots (GQDs) doping of the NiO NPs layer has risen to prominence because it also allows us to explore different functionalisation of the 2D material¹⁵⁹. For instance, Zhang *et al.*¹⁶⁰ showed an improvements in PCE from 14.6% to above 18% on rigid device by chemically reducing the graphene oxide dopant with hydrazine or urea, also demonstrating a 14.1% PCE on plastic substrate. Wang *et al.*¹⁶¹ investigated in details the effect of the functionalising group, finding that hydroxy-functionalised GQDs induced a severe aggregation of the NiO nanoparticles within the precursor ink. At the same time, the amine functionalisation enabled the formation of a smooth and high-quality NiO layer leading to a PCE of 19.55% on a rigid substrate and of above 18% on PEN/ITO and maintaining 88% of PCE after 1000 bending cycles at a diameter of 10mm. Further investigation on the role of functionalised GQDs on the mechanical stability of the flexible devices will be of high interest to consolidate this critical approach. An insightful analysis about the mechanical stability is provided by Cong *et al.*¹⁵², who exploited the e-beam evaporation with a glancing-angle atomic deposition layout (GLAD) to control the morphology of the NiO layer (figure 4a). The process is compatible with plastic substrates, and by varying the glancing angle is possible to cast a compact layer (GA=0°) or a nanopillar array (GA=85°). The optimised nanopillar array increased the Jsc and the FF of the solar cells, and flexible devices with PCE above 17% were demonstrated. Moreover, finite element simulation showed that the presence of the nanopillar array on top of the compact layer reduced the mechanical stress upon bending (figure 4b), directly improving the mechanical stability of the flexible perovskite solar cells.

5.2 Carbon-based Printable Perovskite Solar Cells

Triple mesoscopic stack perovskite solar cells with a printable carbon electrode (c-PSCs) are subject of intense research due to low costs and the promising stability, especially when introducing the 5-AVA into the perovskite composition¹⁶². In c-PSCs, the perovskite is infiltrated through an mp-TiO₂ as electron selective contact and a mesoporous Al₂O₃ or ZrO₂ scaffold. The electrode is printed



carbon, which guarantees higher stability concerning metal electrodes and partially acts as an encapsulating layer. The efficiency of HTM-free c-PSCs, which is the standard configuration, with the carbon electrode also functions as hole contact, is severely hindered by the low Voc and FF. This drawback can be mitigated by introducing a p-type contact¹⁶³. Xu *et al.*¹⁶⁴ observed a net increase in both Jsc (from 14.3mAcm⁻² to 21.3mAcm⁻²) and Voc (from 0.66V to 0.76V) when exploiting the multiple mp-TiO₂/mp-ZrO₂/mp-NiO and a PCE approaching 15%. Improved energetic alignment between perovskite and NiO containing carbon electrode might explain the PCE¹⁶⁵⁻¹⁶⁷. Intensive research was after that dedicated to improving the efficiency of c-PSCs by modifying the NiO layer morphology¹⁶⁸, processing^{169,170} or doping¹⁷¹. Still, more work is required to improve the PCE from about 15% substantially. However, efficiencies above 18% employing printable carbon electrodes have been demonstrated by adopting an n-i-p configuration with P3HT/Graphene¹⁷² or CuSCN¹⁷³ as compact HSL on top of the perovskite, suggesting that future advancement in NiO processing on top of perovskites could enable stable and cheap carbon-based perovskite solar cells with minimal efficiency losses.

5.3 Lead-Free Perovskite Solar Cells

Efficient lead-free perovskite solar cells are now only a matter of time, as confirmed by the certified efficiency of 12.4%¹⁷⁴. It is interesting to note that PEDOT:PSS is the most employed HSL for Sn-based PSCs¹⁷⁵. With lead halide perovskites, one of the driving forces to adopt NiO was the replacement of the relatively unstable PEDOT:PSS^{176,177}. The reasons behind the scarce application of NiO in Sn-PSCs are not known. The prime suspect is that the lower ionisation energy of PEDOT:PSS in respect to NiO might drive a better band alignment with the VB of tin halide perovskites, shallower than Pb counterpart. Another possibility is that the NiOOH-rich surface might induce the Sn²⁺ oxidation to Sn⁴⁺, degrading the interface. Ideally, these two issues might be tackled via interface engineering. The valence band of NiO can be shifted by anchoring molecular dipoles on the surface¹⁴³.

Moreover, molecular monolayers have been proved excellent to protect perovskite surfaces and interfaces¹⁷⁸. We foresee that chemical or physical treatments of NiO surface^{179,180} might also improve the optoelectronic quality of NiO/Sn-Perovskite interface. For instance, NaBH₄ has been proved effective in reducing NiO surface¹⁸¹. This specific research topic is in its infancy, still pioneering results push towards cautious optimism. A 3.31% efficient β -CsSnI₃ PSC employing a sputtered-NiO / spin-coated NiO bi-layer was demonstrated by Wang *et al.*¹⁸² and an efficiency approaching 10% was obtained by Li *et al.*¹⁸³ and Wang *et al.*¹⁵³ (figure 4c).



6. Conclusion and Outlook

The implementation of NiO as hole selective contact in halide perovskite photovoltaics yields power conversion efficiencies above 20%, together with low cost, easy processing and long term stability. The use of NiO nanoparticles will probably be the choice of election for flexible photovoltaics. Here, the synergy with 2D materials can be particularly fruitful by improving mechanical flexibility and reducing energy losses. When considering rigid substrates and tandem photovoltaics, processing by sputtering or spray pyrolysis might be the best choice for easy industrial adoption, with the TCO/NiO substrate processed in the same line. We have discussed in detail that a broad set of dopants can be introduced to enhance the conductivity of NiO or to improve the energy levels alignment with the halide perovskites. We have shown that each dopant act in a different way depending on its size, valence and chemical identity. In our opinion a definitive choice of the best NiO dopant is not possible yet, especially considering the long term stability and the variety of perovskite formulation that can be used. Dopants can segregate at the NiO surface or diffuse inside the perovskite, and the doping stability has to be assessed in greater detail. In addition to that, we showed that pieces of evidence are accumulating stressing out that NiO is particularly reactive for lead halide perovskites. Light, temperature and electrical bias can all trigger the NiO / perovskite reactivity. Thus, aiming at highly efficient and stable solar cells, the introduction of a passivation layer seems mandatory. Self-assembled monolayers can represent the ideal choice to passivate NiO defects, tuning the energy levels and promoting the growth of a high-quality perovskite film. An alternative might be the introduction of an ultra-thin layer (tunnelling layer) of inorganic insulating materials (e.g. MgO, Al₂O₃). Moreover, we believe that careful engineering of NiO surface will enable efficient and stable lead-free perovskite solar cells.

Conflicts of Interest

There are no conflicts of interest to declare.

Acknowledgments

D.D.G. acknowledges the PhD program of the Department of Chemistry of La Sapienza University of Rome for funding. D.D. acknowledges the financial support from MIUR (Project PRIN 2017 with title: Novel Multilayered and Micro-Machined Electrode Nano-Architectures for Electrocatalytic Applications- Prot. 2017YH9MRK). D.D. acknowledges also the financial support from the University of Rome LA SAPIENZA [Project ATENEO 2019 Prot.RM11916B756961CA].



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DOI: 10.1039/D0SC02859B