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Straightforward and green synthesis of all-inorganic CsPbI₃ perovskite solar cells *via* nickel acetate incorporation

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Research on stable inorganic perovskite CsPbI₃ has emerged as a promising alternative to organic–inorganic hybrid perovskites due to its notable thermal stability and suitable bandgap (~1.73 eV) for single-junction and tandem solar cells in both indoor and outdoor applications. However, CsPbI₃ films with large grains and low trap densities are required to achieve high-performance and stable perovskite solar cells. In this study, we present a novel synthetic strategy in which nickel acetate (Ni(AcO)₂·4H₂O) is incorporated in a pure DMSO CsPbI₃ precursor solution leading to the formation of stable γ -CsPbI₃ (black phase) nanocomposite perovskite films, as evidenced by XRD analysis. Moreover, the absence of detectable residual PbI₂ further confirms the enhanced conversion efficiency facilitated by Ni(AcO)₂ addition in our target when compared with pure CsPbI₃. Using this DMAI/HI-free approach, our top device with 0.1 M Ni(AcO)₂ (7.1 mol%) achieves over 12% power conversion efficiency in n–i–p mesoscopic configuration, with a lifespan exceeding 600 hours at maximum power point (MPP) and minimal losses (<20%) without encapsulation under controlled inert atmosphere. Besides, efficiencies over 15 and 17% are achieved under cool and warm white low-intensity illumination conditions, respectively, underscoring its potential for energy harvesting in indoor environments. The life cycle assessment (LCA) indicates that this new synthesis strategy reduces global warming potential (GWP) by 70% and eliminates hazardous chemicals like DMF and toluene. However, Ni(AcO)₂ and PbI₂ remain in the absorbing layer, requiring careful consideration.

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Broader context

Perovskite solar cells (PSCs) are rapidly advancing as a leading candidate for next-generation photovoltaic technologies. However, most state-of-the-art PSCs rely on organic–inorganic hybrid halide perovskites, which suffer from long-term stability issues, and rely on toxic solvents during fabrication. All-inorganic perovskites like CsPbI₃ offer superior thermal stability and are particularly promising for both outdoor and indoor energy harvesting applications, but their practical implementation has been hindered by phase instability and challenges in achieving high-quality films. This work addresses those challenges by introducing a new, environmentally friendly synthesis method using nickel acetate as a phase-directing additive in a DMF- and antisolvent-free formulation. The resulting γ -CsPbI₃ films exhibit improved crystallinity and enhanced stability, solar cells with efficiencies >12% without further passivation. Furthermore, the use of a greener fabrication route reduces the global warming potential by 70%, demonstrating that efficient and stable perovskite devices can be achieved without compromising environmental safety. These findings contribute to the ongoing transition toward sustainable and scalable PSC technologies, and highlight the potential of inorganic perovskites for clean energy generation beyond conventional settings.

Introduction

The interest in organic–inorganic halide perovskite solar cells (PSCs) has surged within the photovoltaics community, primarily driven by their impressive power conversion efficiencies (PCE) and the potential for low-cost facile fabrication processes. Since their debut in 2009, when initial efficiencies were a modest 3–4%,¹ advancements in this technology have rapidly increased PCE values, with the highest certified efficiency now reaching 26.1%.² These materials typically feature a structure consisting of organic and inorganic cations like

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methylammonium (MA^+), formamidinium (FA^+), and cesium (Cs^+) within a lead halide framework. However, despite their high efficiency, these hybrid perovskite structures are plagued by stability issues that undermine their long-term viability. In terms of commercialization, solar modules must endure wide operational stress factors such as temperature, light exposure (visible and UV), and electrical bias (outlined in the standard ISOS stability protocols), as these are critical concerns for their stability.³⁻⁷

In recent years, fully inorganic cesium lead halide perovskites, and particularly CsPbI_3 , have emerged as a potential candidate due to their exceptional thermal stability.⁸⁻¹² CsPbI_3 is especially promising due to its bandgap of 1.73 eV, making it suitable for applications in double-junction perovskite/silicon tandem solar cells in both indoor and outdoor photovoltaic applications.^{3,13-15} The maximum theoretical efficiency under varying light conditions can be determined by adapting the Shockley–Queisser limit to different irradiation spectra.¹⁶ Notably, this efficiency limit increases from 33% under sunlight illumination to 57% under indoor lighting conditions.¹⁷

The current best research PCEs for these all-inorganic perovskite absorbers are around 21%.^{18,19} However, CsPbI_3 faces significant challenges in maintaining a stable perovskite phase at ambient temperatures due to the small ionic radius of cesium, which results in structural instability. This structural instability poses a significant drawback for long-term photovoltaic applications.²⁰ Furthermore, certain synthetic routes require annealing temperatures exceeding 350 °C to achieve the α - CsPbI_3 phase, rendering it impractical for use with various device architectures, including different substrates and charge transport layers.^{15,21,22} In this sense, low-temperature processing benefits tandem solar cell fabrication, reducing energy consumption, simplifying operation, improving reproducibility, and enabling sustainable industrial scalability.¹⁴

Innovations in material processing and stabilization methods have paved the way for obtaining CsPbI_3 perovskite black phases at lower temperatures to become a viable alternative to their hybrid counterparts, offering a path toward more thermally stable and efficient photovoltaic technologies. The different reported strategies to stabilize CsPbI_3 black phases include solvent engineering,^{23,24} surface passivation engineering modifying the surface tension,²⁵ dimensionality engineering (scaffold confinement,²⁶ nanocrystal colloidal approaches¹¹ and quasi-2D by incorporating large organic cations^{27,28}) or chemical engineering (small molecules²⁹⁻³³ and ionic incorporation partially replacing lead with other divalent cations ($\text{CsPb}_x\text{M}_{1-x}\text{I}_3$)^{34,35} or substituting some iodide with bromide³⁶). Among them, the most widespread one for the fabrication of high-efficiency PSCs at relatively low temperature relies on the addition of dimethylammonium iodide (DMAI) as $(\text{DMA}_x\text{Cs}_{1-x})\text{PbI}_3$. DMAI has demonstrated the ability to stabilize and influence the crystallinity and grain size of the CsPbI_3 perovskite black phases.³³ This was first reported by Eperon *et al.* 2015 who introduced hydroiodic acid (HI) as an additive³⁷ that, in subsequent studies, was identified to generate *in situ* DMAI as a decomposition product of DMF through acidic hydrolysis catalyzed by HI.³⁸ Although high annealing temperatures are sometimes necessary to fully

volatilize the organic additives and promote phase transitions in CsPbI_3 ,³⁹ many high-efficiency devices exceeding 20% power conversion efficiency are fabricated by incorporating DMAI, which aid in phase stabilization during processing.^{20,40,41} In this scenario, there is still ongoing debate about whether DMAI-assisted CsPbI_3 perovskites are fully inorganic materials or instead represent $\text{Cs}_{1-x}\text{DMA}_x\text{PbI}_3$ mixed-cation or “cesium-rich” systems.^{42,43}

Recently, we have demonstrated the potential of a nickel acetate-based matrix for the *in situ* synthesis and stabilization of perovskite nanocrystals through a simple and efficient process.⁴⁴⁻⁴⁸ In this approach, nanocrystal size was primarily controlled by adjusting the relative concentrations of perovskite precursors and $\text{Ni}(\text{AcO})_2$, as well as factors such as relative humidity during synthesis. Expanding on these findings, we investigated $\text{Ni}(\text{AcO})_2$ for the synthesis of large-grain perovskites for photovoltaics, particularly for materials with metastable polymorphic phases like the γ - CsPbI_3 black phase. We present a promising DMSO-only, DMAI/HI-free precursor solution strategy incorporating $\text{Ni}(\text{AcO})_2$ to drive the crystallization and stabilization of γ - CsPbI_3 in a nanocomposite. Our results show that increasing grain size to a level suitable for photovoltaic applications requires an excess of perovskite precursors with respect to $\text{Ni}(\text{AcO})_2$. We demonstrate a significant correlation between the concentration of $\text{Ni}(\text{AcO})_2$ and the stabilization of the γ - CsPbI_3 black phase in comparison with pristine CsPbI_3 . As confirmed through X-ray diffraction (XRD) analysis, the role of $\text{Ni}(\text{AcO})_2$ directly impacts the crystallization process. EDX analysis also confirms a homogeneous distribution of $\text{Ni}(\text{AcO})_2$ around the perovskite grains. Through SEM, we observe the effect of the annealing temperature and concentration impacting the grain size in the perovskite absorber layer. JV curves further confirm a $\text{Ni}(\text{AcO})_2$ concentration threshold for optimal device performance without compromising the charge extraction. Finally, using this method, our best device, containing 0.1 M $\text{Ni}(\text{AcO})_2$ (7.1 mol%), achieves a power conversion efficiency (PCE) of over 12% in n-i-p configuration without any passivation or surface modification, maintaining a lifespan of more than 600 hours at maximum power point (MPP) with minimal losses below 20%. Besides, its adequacy to work under enhanced low-intensity lighting conditions has been tested, achieving PCEs over 15 and 17% under cool and warm white illuminations, respectively. The life cycle assessment (LCA) indicates that the approach reduces global warming potential (GWP) by 70% and minimizes impacts across most categories, despite the inclusion of $\text{Ni}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$, which has low toxicity compared to PbI_2 . Furthermore, the DMSO-only, DMAI/HI-free approach avoids hazardous substances like DMF, toluene, and TOPO (used in a comparative synthesis approach). However, caution is warranted as $\text{Ni}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ and PbI_2 remain in the absorbing layer.

Results and discussion

In situ synthesis of CsPbI_3 -nanocomposite films

γ - CsPbI_3 nanocomposite films are synthesized by a solution-based approach from a precursor solution of CsI, PbI_2 , and



$\text{Ni}(\text{AcO})_2$ in DMSO. The precursor solution is spin-coated onto a substrate, followed by rapid thermal annealing to crystallize the γ - CsPbI_3 phase. Fig. 1 provides an overview of the general *in situ* synthesis process for the nanocomposite, illustrating the synthetic approach for CsPbI_3 and highlighting the effect of $\text{Ni}(\text{AcO})_2$ on the perovskite nanocomposite crystallization.

Achieving an optimal grain size for photovoltaic applications necessitates an excess of perovskite precursors relative to $\text{Ni}(\text{AcO})_2$. Excess $\text{Ni}(\text{AcO})_2$ can limit the growth of large grains by disrupting the perovskite framework. A controlled precursor ratio is, therefore, critical to balancing grain growth while maintaining structural stability. Therefore, we have tested different $\text{Ni}(\text{AcO})_2$ concentrations ranging from 3.7 to 38.1 mol% within CsPbI_3 , ensuring an excess of perovskite in the final film. This approach allowed us to systematically evaluate the impact of $\text{Ni}(\text{AcO})_2$ on the crystallization process, lattice structure, grain growth, and stability of CsPbI_3 .

Optical properties of the nanocomposite perovskite films

The effect of $\text{Ni}(\text{AcO})_2$ concentration and annealing times on the optical properties of the perovskite films are studied at an annealing temperature of 200 °C. For all evaluated conditions, the CsPbI_3 concentration is kept constant at 1.3 M to ensure a consistent assessment of the effects of $\text{Ni}(\text{AcO})_2$ concentration on the final layer properties. We first examined the annealing time at 200 °C, a temperature slightly above the boiling point of DMSO (189 °C), to ensure its effective removal and a complete phase transition to γ - CsPbI_3 phase.⁹

Fig. 2a shows films prepared with different $\text{Ni}(\text{AcO})_2$ concentrations and various annealing times at 200 °C. For all concentrations, the formation of the γ -phase is observed after just 5 s, indicating a rapid crystallization to the γ - CsPbI_3 phase. However, as the annealing time increases, films with a $\text{Ni}(\text{AcO})_2$ concentration of 0.05 M (3.7 mol%) change from black to yellow, suggesting the transformation to the non-perovskite yellow phase. In contrast, from concentrations 0.1 M (7.1 mol%) and higher, the γ -phase remains stable for longer

bake times, indicating $\text{Ni}(\text{AcO})_2$ improves not only γ - CsPbI_3 crystallization but also the γ -phase stability.

UV-vis spectroscopy confirms the fast crystallization of the black γ - CsPbI_3 phase for samples baked at 200 °C in the presence of $\text{Ni}(\text{AcO})_2$. After just 5 seconds, we observe the characteristic absorption band at 680 nm corresponding to γ - CsPbI_3 in all samples with $\text{Ni}(\text{AcO})_2$ (Fig. 2b). The control sample without $\text{Ni}(\text{AcO})_2$ does not crystallize into the γ - CsPbI_3 (Fig. 2c). The excitonic band intensity increases with the annealing time. For a 0.1 M $\text{Ni}(\text{AcO})_2$ (7.1 mol%), we observe the absorption excitonic band reaching its maximum at 10 s. However, for longer baking times, 20 s, phase degradation occurs, leading to the formation of the non-perovskite yellow phase (δ - CsPbI_3), and a decrease in the absorption band (Fig. 2b). A comparison of their optical properties between pristine CsPbI_3 and γ - CsPbI_3 - $\text{Ni}(\text{AcO})_2$ nanocomposite is shown in Fig. 2c. As expected, the pristine δ - CsPbI_3 does not display photoluminescence (PL), whereas the γ - CsPbI_3 - $\text{Ni}(\text{AcO})_2$ nanocomposite exhibits a PL peak centered at approximately 720 nm. The same trend is observed for different concentrations of $\text{Ni}(\text{AcO})_2$. However, at 0.05 M $\text{Ni}(\text{AcO})_2$ (3.7 mol%), a partial transformation of γ - CsPbI_3 is initially observed, but the yellow δ -phase forms after a few seconds (see Fig. 2a), which is further confirmed by XRD in the structural characterization section. This confirms that $\text{Ni}(\text{AcO})_2$ plays a determining role in the crystallization and stability of γ - CsPbI_3 . The optimal composition is 1.3 M CsPbI_3 : 0.1 M $\text{Ni}(\text{AcO})_2$ (92.9 mol% CsPbI_3 and 7.1 mol% $\text{Ni}(\text{AcO})_2$), annealed at 200 °C for 10 s. This concentration has been identified as a critical threshold for maintaining both crystallinity and stability, as further confirmed in the photovoltaic performance (see device characterization section, *J-V* curves, Fig. 4b). Beyond this threshold, the current density significantly declines faster, attributed to reduced charge carrier mobility associated with the excessive $\text{Ni}(\text{AcO})_2$ content. This leads to poor grain interconnectivity, which significantly hinders its suitability for application as PSCs, as detailed in the subsequent sections.

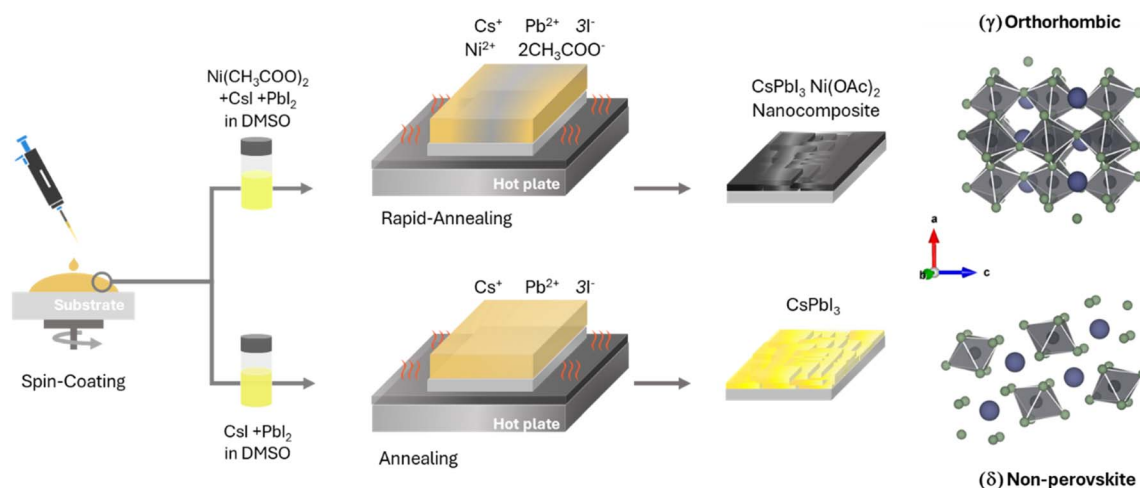


Fig. 1 Synthetic approach for CsPbI_3 nanocomposites, emphasizing the impact of $\text{Ni}(\text{AcO})_2$ doping on perovskite crystallization.



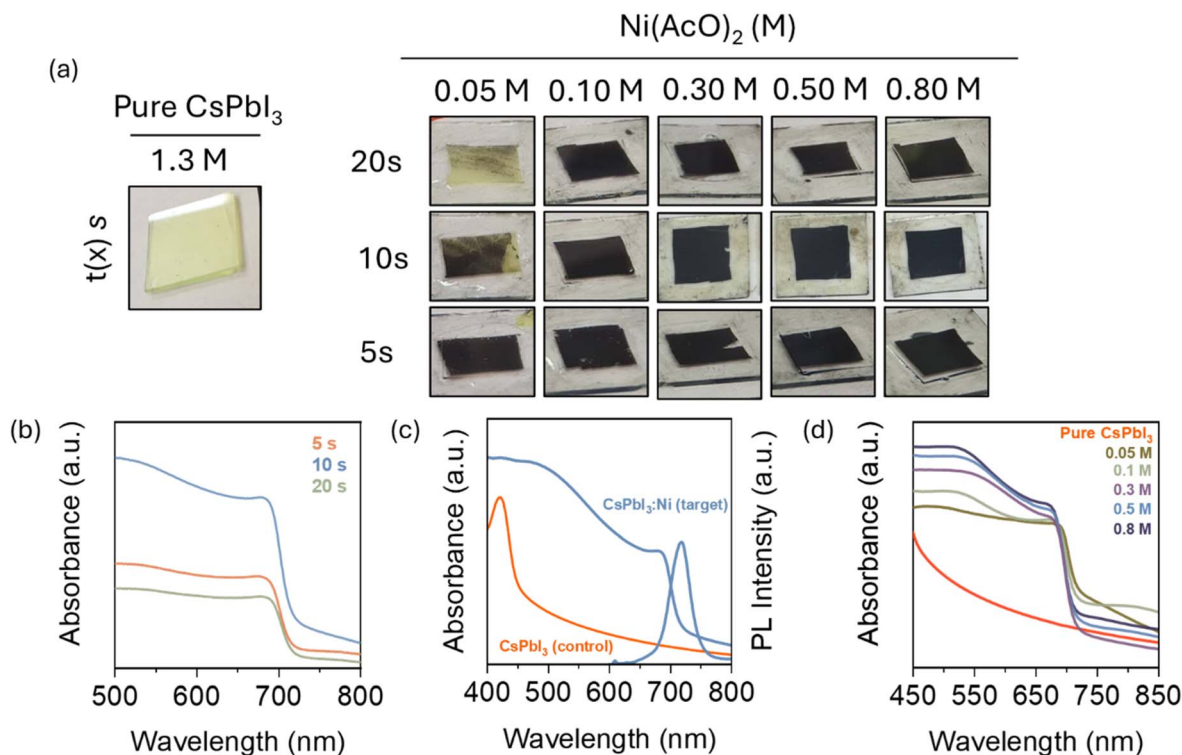


Fig. 2 Impact of annealing time and concentration on CsPbI₃ films. (a) Photographic images of pristine CsPbI₃ and CsPbI₃-Ni(AcO)₂ films annealed at 200 °C for different times and Ni(AcO)₂ concentrations. (b) Annealing time dependency in UV-vis absorption spectra for 0.1 M (7.1 mol%) Ni(AcO)₂ concentration. (c) UV-vis absorption spectra and PL spectra comparison for the control and the target nanocomposite annealed at 200 °C for 10 s. (d) Nanocomposite UV-vis absorption spectra vs. Ni(AcO)₂ concentration annealed at 200 °C for 10 s.

We have calculated the optical bandgap (E_g) of γ -CsPbI₃-Ni(AcO)₂ nanocomposite thin films from Fig. 2d by simulating the absorption spectra near the band edge using Elliott's formula (see SI).⁴⁹ The absorption spectra (Fig. S1) shows that increasing the Ni(AcO)₂ concentration shifts the optical E_g to higher energies (Table S1). This shift is attributed to significant random microstrain⁵⁰ within the perovskite grains, as evidenced by the broadening of XRD peaks, which will be discussed in the following section. This strain plays a crucial role in stabilizing the γ -CsPbI₃ phase, a topic explored further in the next section.

Structural and morphological characterization

The concentration of Ni(AcO)₂ plays a crucial role in modulating the optical properties of γ -CsPbI₃. To investigate this effect, we have conducted XRD analyses of CsPbI₃ nanocomposites synthesized with varying Ni(AcO)₂ concentrations at different annealing temperatures to determine the optimal conditions for γ -CsPbI₃ formation. The XRD diffractograms (Fig. 3) reveal how annealing temperature influences the crystallinity of the γ -CsPbI₃ phase, effectively suppressing transitions to the non-perovskite δ -phase (Fig. 3a). These structural insights align well with the observed optical properties.

For all temperatures, we found characteristic peaks corresponding to the orthorhombic γ -phase near 14.3°, 20.8°, and 28.9°, which can be assigned to the (020), (002), and (202) planes, respectively (ICSD no. 434 338). At 250 °C, a phase

transition is observed, evidenced by the appearance of a weak diffraction peak at 13.1°, which corresponds to the (102) plane of the δ -CsPbI₃ phase (Fig. 3b) (ICSD no. 250744).

Regarding the crystallization mechanism, we observe the formation of an intermediate 0D Cs₄PbI₆ phase at lower temperatures. As shown in Fig. 3c, the characteristic peaks of the 0D Cs₄PbI₆ phase at 11.9° and 28.6° at 100 and 150 °C, disappear at higher temperatures. This observation suggests that Cs₄PbI₆ acts as a template in the phase conversion of CsPbI₃. This is consistent with a study of an intermediate formamidinium acetate by Duan *et al.* 2022.³² At 200 °C, the 0D intermediate phase is fully removed, leaving only the γ -CsPbI₃ phase. These observations align with our previous findings, which highlighted the role of the Ni(AcO)₂ in the transformation of a 0D intermediate phase to the corresponding 3D perovskite phase by the presence of acetate groups.⁴⁷

We observe that higher temperatures improve crystallinity and peak intensity. As observed in SEM, annealing at 200 °C promotes the formation of larger γ -CsPbI₃ grains, which is favorable for enhancing carrier mobility and overall device performance.⁵¹ Therefore 200 °C is the optimal temperature target for synthesizing γ -CsPbI₃.

The formation of the γ -CsPbI₃ phase is also strongly influenced by the amount of Ni(AcO)₂. The effect of Ni(AcO)₂ concentration is also examined in samples annealed at 200 °C for 10 s. XRD diffractograms of films with Ni(AcO)₂ concentrations below 0.1 M (7.1 mol%) reveal residual peaks of the δ -



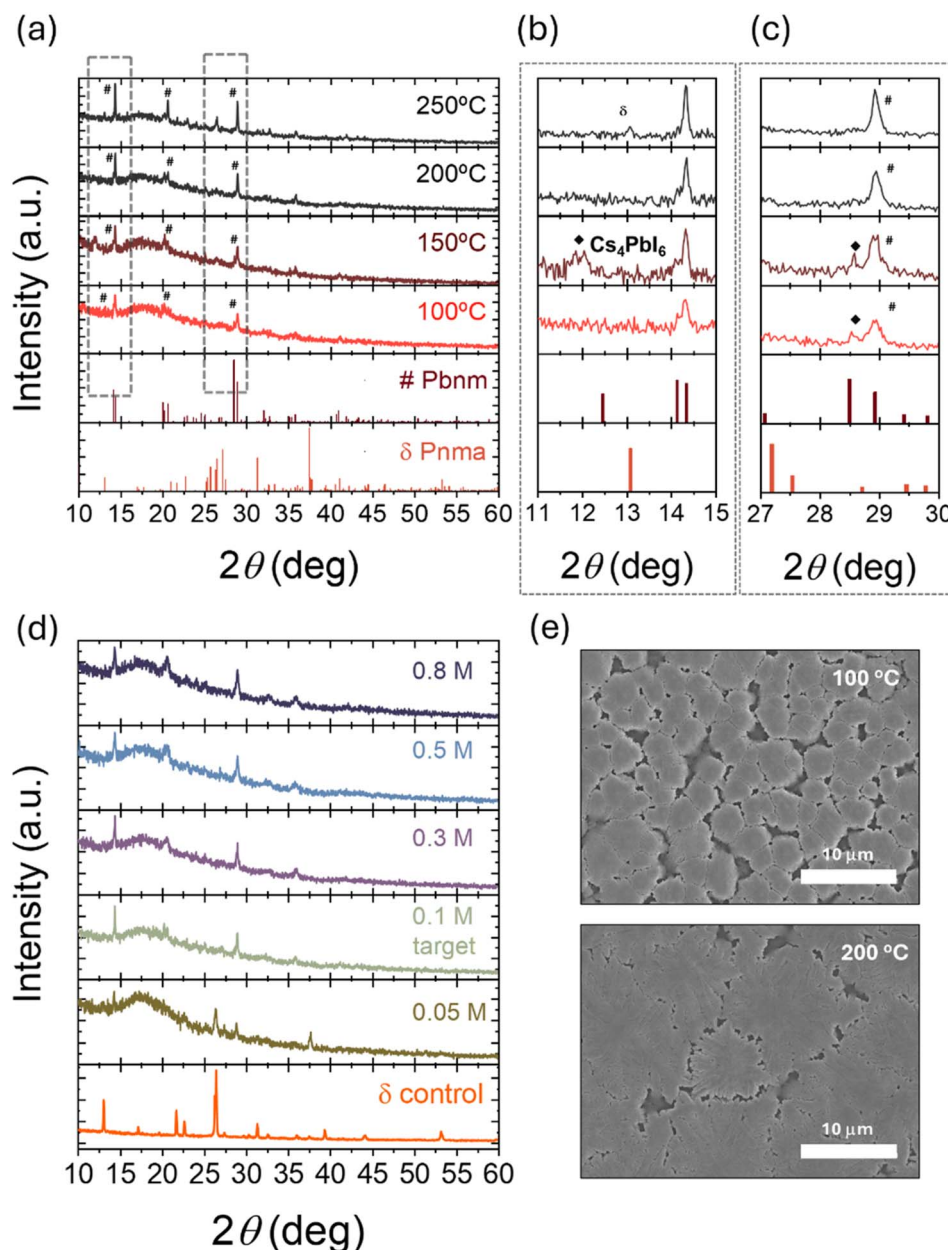


Fig. 3 XRD patterns of $\text{CsPbI}_3\text{-Ni}(\text{AcO})_2$ nanocomposites. (a–c) Annealing temperature impact on 0.1 M $\text{Ni}(\text{AcO})_2$ for 10 s. (d) Effect of $\text{Ni}(\text{AcO})_2$ concentration annealed at 200 °C for 10 s. (e) SEM images of 0.1 M $\text{Ni}(\text{AcO})_2$ nanocomposite at 100 and 200 °C for 10 s.

phase, indicating an incomplete phase transition or poor stabilization of the $\gamma\text{-CsPbI}_3$ phase (Fig. 3d). When the concentration exceeds 0.1 M (7.1 mol%), the orthorhombic peaks become more intense and sharper, indicating improved crystallinity (Fig. 3d).

The role of Ni^{2+} in the crystallographic structure can also be assessed in this context. Partial exchange of Pb^{2+} (~ 120 pm) with smaller Ni^{2+} (~ 72 pm) would typically induce lattice contraction, resulting in a shift of XRD peaks to higher 2θ values. However, the absence of a significant shift eliminates the possibility of partial substitution within the CsPbI_3 lattice and makes it highly unlikely.⁵²

A detailed analysis of peak broadening for different $\text{Ni}(\text{AcO})_2$ concentrations has been conducted. The crystallite size (D) and

microstrain (ϵ) are determined using Williamson–Hall plots (Fig. S2). Increasing the $\text{Ni}(\text{AcO})_2$ concentration from 0.05 to 0.8 M (3.7 to 38.1 mol%) leads to a reduction in grain domain size from 61 to 30 nm, together with a corresponding increase in microstrain.⁵⁰ The microstrain induced by $\text{Ni}(\text{AcO})_2$ incorporation kinetically hinders the transformation from the γ to the δ -phase, enhancing phase stability as $\text{Ni}(\text{AcO})_2$ concentration increases. This trend is consistent with Elliott's bandgap calculations (Table S1), which indicate a shift toward higher energies with increasing $\text{Ni}(\text{AcO})_2$ concentration, and with the SEM images, which show a decrease in particle size as the $\text{Ni}(\text{AcO})_2$ content increases (Fig. S4). This suggests that the presence of acetate could facilitate the formation of additional



nucleation sites of the γ -CsPbI₃ and, consequently, lead to a narrower grain size distribution in the perovskite films.

Additionally, to assess the structural stability of CsPbI₃ perovskite films incorporating Ni(AcO)₂ under ambient conditions, we have conducted time-resolved XRD of target CsPbI₃ film exposed to 60% RH at 25 °C measuring samples immediately after glovebox removal and every 10 minutes thereafter (Fig. S3). Fresh films exhibit a single peak at 14.3°, corresponding exclusively to the γ -CsPbI₃ phase, with no secondary phases detected. Over time, new peaks at \sim 9.8° and \sim 12.9° appear, corresponding to the δ -CsPbI₃ phase and PbI₂, respectively. This indicates moisture-driven degradation of the perovskite structure toward more thermodynamically stable phases, while preserving the γ -CsPbI₃ phase under inert conditions, emphasizing the impact of humidity on film stability.

Scanning Electron Microscopy (SEM) images (Fig. 3e) revealed significant differences in the microstructure and morphology of the nanocomposite for 100 °C and 200 °C annealing temperature. We observe the formation of larger grains and more compact films at 200 °C. We attribute the reduced grain size at lower temperatures to incomplete crystallization of perovskite due to inefficient DMSO removal. Larger grains and more compact films are advantageous for device performance by reducing grain boundary defects and consequently minimizing recombination centers and enhancing charge carriers mobility.²¹

Energy-dispersive X-ray (EDX) analysis (Fig. S5) further corroborates the uniform distribution of Ni(AcO)₂ across the perovskite grains. Elemental mapping reveals a consistent presence of Ni homogeneously distributed throughout the entire grain structure, with no noticeable aggregation or phase separation. This homogeneity suggests that Ni²⁺ is primarily localized around the perovskite grains rather than substituting within the crystal lattice. This conclusion aligns with the XRD results, where the crystallographic peaks remain unchanged, indicating that Ni²⁺ does not significantly alter the perovskite structure but instead surrounds the grains. This distribution may play a key role in enhancing the material's stability and influencing its electronic properties.

XPS analysis has been conducted to investigate the variation in lattice binding energy of CsPbI₃ with and without Ni(AcO)₂ (Fig. S6). The Cs 3d, Pb 4f, and I 3d peaks consistently shift to lower binding energies upon the addition of Ni(AcO)₂. This shift can be attributed to an increase in electron density on the surface of CsPbI₃, due likely to electron transfer from Ni atoms to the perovskite lattice. The increased surface charge density induced by Ni(AcO)₂ addition reduces the surface tension of CsPbI₃, consequently lowering the surface free energy.²⁹ This modification plays a crucial role in stabilizing the γ -CsPbI₃ phase in our synthesis approach.

To gain broader insight into the role of acetate salts in stabilizing γ -CsPbI₃ beyond Ni(AcO)₂, preliminary fundamental studies have been conducted exploring the use of alternative metal acetates under identical DMSO only synthesis route. Specifically, Co(AcO)₂·4H₂O and Zn(AcO)₂·2H₂O have been evaluated alongside Ni(AcO)₂ to assess how the nature of the metal and acetate group influence the optical, structural, and

morphological properties of the resulting perovskite films (Fig. S7). The Co(AcO)₂-based γ -CsPbI₃ film exhibits a very similar absorption profile, closely matching that of Ni(AcO)₂ in both onset and shape, suggesting comparable optical quality and phase formation (see Fig. S7a). In contrast, the film with Zn(AcO)₂ shows a less pronounced excitonic feature and a blue-shifted absorption onset, indicating poorer crystallinity or the presence of a different phase. XRD patterns (Fig. S7b) revealed that both Co and Zn acetates promoted partial γ -phase formation, though residual δ -phase and PbI₂ reflections persisted. SEM images (Fig. S7c) show moderately cohesive grains for Co(AcO)₂ and poorly cohesive grains for Zn(AcO)₂. We hypothesize that stabilization arises from a combination of factors, including waters of crystallization, acetate ligand basicity, and salt hygroscopicity.⁴⁷ While these findings provide valuable insights into the role of metal acetates in phase stabilization, further detailed investigations will be essential to fully elucidate the underlying mechanisms and optimize material performance.

Photovoltaic characterization

We tested the performance of CsPbI₃-Ni(AcO)₂ devices in n-i-p configuration for different Ni(AcO)₂ concentrations. The device structure consisted of FTO/c-TiO₂/m-TiO₂/perovskite/Spiro-OMeTAD/Au (Fig. 4a). A cross-section image of the complete device stack is provided in the SI (Fig. S8). Fig. 4b shows the statistical data of different devices prepared from 0.05 to 0.8 M Ni(AcO)₂ (3.7 to 38.1 mol%). Across a range of concentrations, the curves show a volcano-shaped dependence on concentration. The best photovoltaic performance is achieved for 0.1 M Ni(AcO)₂. The champion SC has J_{sc} , V_{oc} , and FF values of 17.6 mA cm⁻², 1.03 V, and 68.13%, respectively, corresponding to a PCE of 12.43%. The J - V curve and statistics are shown in Fig. 4c. These findings are in good agreement with XRD results: at 0.05 M Ni(AcO)₂, both δ -CsPbI₃ and γ -CsPbI₃ phase perovskite phases coexist. The non-perovskite δ -CsPbI₃ phase avoids an effective charge transport within the absorber, leading to non-optimal electrical performance. Similarly, above 0.1 M Ni(AcO)₂ (7.1 mol%), we observe a rapid drop in the current density. While a higher Ni(AcO)₂ concentration enhances the stability of the orthorhombic γ -CsPbI₃ phase (see Fig. S9), photovoltaic performance is compromised. We attribute the decrease in PV performance to the active role of Ni(AcO)₂ in stabilizing the γ -CsPbI₃ phase while simultaneously promoting the separation of perovskite grains. Because Ni(AcO)₂ is an insulating material, the resulting composite shows a poorer electrical interconnection among grains, which hinders charge extraction. EDX analysis (Fig. S5) further supports this interpretation by confirming the uniform distribution of Ni(AcO)₂ around the perovskite grains. This phenomenon has been previously observed in studies involving Ni(AcO)₂ matrices.⁴⁶

In addition, we have conducted a light stability test on an unencapsulated device under ambient conditions in an inert nitrogen atmosphere, with constant 1-sun illumination. The target CsPbI₃-Ni(AcO)₂ device maintained approximately 80% of its initial efficiency after 600 hours of continuous light exposure measured at a fixed voltage near the MPP (Fig. 4d).



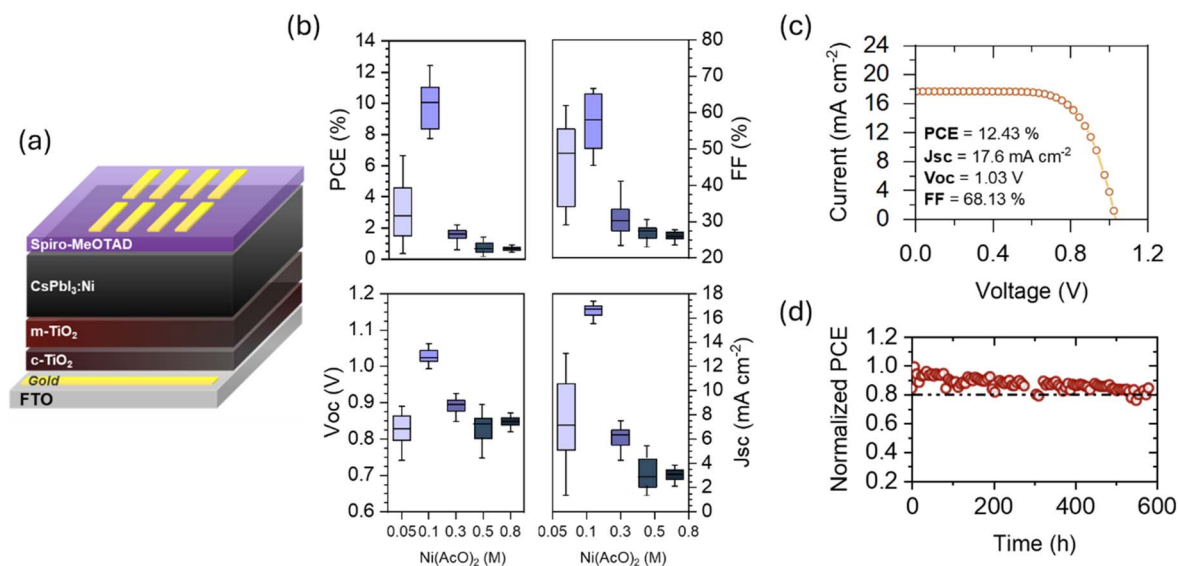


Fig. 4 (a) Device structure: FTO/c-TiO₂/m-TiO₂/CsPbI₃: Ni(AcO)₂/Spiro-OMeTAD/Au. (b) Statistical data of devices with different CsPbI₃: Ni(AcO)₂ ratios. (c) *J*-*V* curve of the champion device. (d) Light stability test on unencapsulated devices under N₂ conditions, with constant 1-sun illumination at 30 °C.

Additional analysis is conducted to investigate the ideality factor (n_{id}) of the solar cells studied at different Ni(AcO)₂ concentrations, providing deeper insights into the dominant recombination mechanisms influencing device performance. The ideality factor is determined from the dependence of the open-circuit voltage V_{OC} on light intensity, as described in Fig. S10.⁵³ At low concentrations of Ni(AcO)₂ (0.05 M), the ideality factor reaches 2.2, indicating dominant trap-assisted recombination and poor material quality, primarily attributed to the coexistence of both delta and gamma phases. For higher Ni(AcO)₂ concentrations (0.1 M) the ideality factor decreases to 1.7, suggesting Shockley-Read-Hall (SRH) recombination within the bulk as the dominant loss mechanism, which aligns with previously reported observations on CsPbI₃ solar cells.⁵³⁻⁵⁵ When increasing Ni(AcO)₂ concentrations to 0.3 M, the ideality factor further decreases to ~ 1.5 . However, this reduction coincides with deteriorated device performance, suggesting the emergence of interfacial recombination issues that correlate with charge transport limitations at higher Ni(AcO)₂ concentrations, as discussed previously.

Low-intensity illumination studies

To explore the potential of this synthesis approach, performance measurements have been conducted on the optimum γ -

Table 1 PSC parameters upon exposure to different light conditions of γ -CsPbI₃-Ni(AcO)₂ nanocomposite solar cell (7.1 mol% Ni(AcO)₂)

Illumination conditions	PCE (%)	FF (%)	J_{sc} (mA cm ⁻²)	V_{oc} (V)
1 Sun (100 mW cm ⁻²)	10.0	70	14.2	1.02
Cool white (23 mW cm ⁻²)	15.4	71	5.3	0.96
Warm white (13 mW cm ⁻²)	17.6	76	3.2	0.94

CsPbI₃-Ni(AcO)₂ nanocomposite solar cell under both cool white and warm white low-intensity illumination. These enhanced indoor light sources with different irradiance spectra (Fig. S11a) achieve peak efficiencies with semiconductor materials featuring bandgaps between 1.7 and 1.8 eV (Fig. S11b), in contrast to the optimal 1.4 eV bandgap for solar illumination. In this context, our best CsPbI₃-Ni(AcO)₂ devices achieve remarkable efficiencies of 15.4% under commercial based cool white (23 mW cm⁻²) and 17.6% under warm white (13 mW cm⁻²) lighting. PSC parameters and *J*-*V* curves for low-intensity illumination measurements are gathered in Table 1 and Fig. 5, respectively. These results further confirm the potential of all-inorganic CsPbI₃-based perovskites for indoor applications, demonstrating strong alignment with theoretical efficiency predictions.

Life cycle assessment

The environmental impacts associated with the synthesis and deposition process of CsPbI₃ with Ni(AcO)₂ are evaluated using the LCA methodology, conducted in accordance with EN-ISO standards (14 040/14 044) and the IEA PVPS guidelines.⁵⁶ This evaluation is juxtaposed with that of the synthesis and deposition of CsPbI₃ with DMAI.⁵⁷

The functional unit for both cases is 1 cm². The absorber layer is the only one considered in the indoor solar cell. The electron and hole transport layer, electrodes, and substrate are the same for the two methods, so they are not included in the comparative assessment. The SI note presents life cycle inventories and evaluation impacts with the method Environmental Footprint, EF 3.0.⁵⁸

The addition of Ni(AcO)₂ to the CsPbI₃ solution avoids the use of several harmful substances compared to the DMAI method: DMAI, MACl, OAI and TOPO.⁵⁷ The number of spin coating processes employed is reduced from 4 to 1, the heating



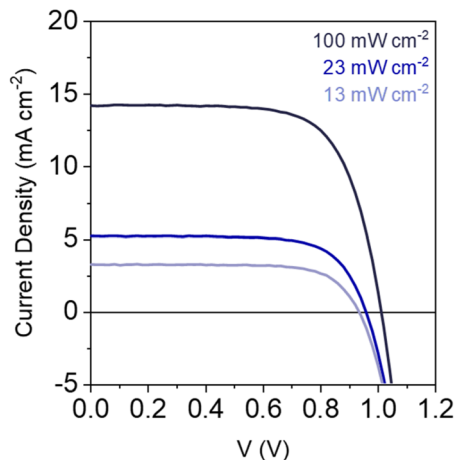


Fig. 5 J - V curves under different light conditions of target CsPbI_3 - $\text{Ni}(\text{AcO})_2$ PSCs.

times for precursor formation are shorter, and the times and temperatures for annealing are also lower. In particular, the energy consumption is 2.6 times higher with DMAI than with the addition of $\text{Ni}(\text{AcO})_2$. However, the metal usage slightly increases for samples using a 0.8 M $\text{Ni}(\text{AcO})_2$ (38.1 mol%) because of the addition of $\text{Ni}(\text{AcO})_2$ and the higher consumption of Pb and Cs. The relative differences between the two methods are shown in the Fig. 6a.

The reduction in material and energy consumption, as well as the decrease in waste generated during spin coating, has a highly positive impact on mitigating climate change (GW), as shown in Fig. 6b, with an overall reduction of 70%. The reduction in environmental impacts is not only produced for the climate change category but for most impact categories (Fig. 6c), with an average impact reduction of 52%. The exception is the category of mineral resource use and metals (Rum) because the consumption of metals has slightly increased. The impacts considered are from cradle to gate, but if, in addition, greater stabilities and/or efficiencies are achieved with the new method, the reduction in environmental impact over the entire life cycle will be even more significant.

The impacts on human toxicity are also reduced, although to a lesser extent than in other impact categories. The synthesis of PbI_2 is primarily responsible for the impacts in these categories, as shown in Fig. 6d. In contrast, the manufacture of $\text{Ni}(\text{AcO})_2$ accounts for only 5% of the impact in the carcinogenic human toxicity category and 2% in the non-carcinogenic human toxicity category.

In addition to the LCA, properties of concern according to harmonized classification and labeling (CLH) or notifications on classification, labeling, and packaging of substances and mixtures (CLP) (consolidated version of EC regulation no. 1272/2008) have also been considered. Lead iodide is the only substance of concern, “toxic for reproduction” (CLH), which is

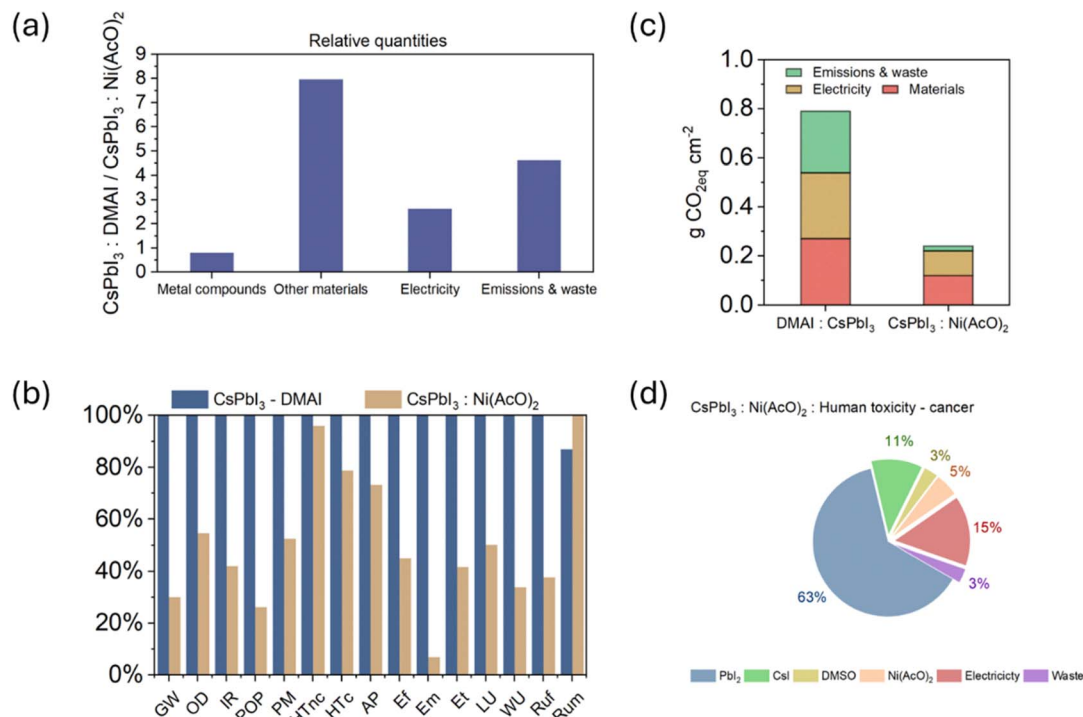


Fig. 6 (a) Relative quantities of materials, energy and wastes for 1 cm^2 of CsPbI_3 synthesized with DMAI in comparison with CsPbI_3 - $\text{Ni}(\text{AcO})_2$. (b) Comparison of absolute climate change impacts broken down into materials, electricity, emissions and waste. (c) Relative impacts for the two methods to synthesize CsPbI_3 (absolute values and meaning of abbreviations are listed in the Table S11). (d) Breakdown of the potential human toxicity-cancer impact for CsPbI_3 - $\text{Ni}(\text{AcO})_2$, whose contribution is only 5% of the total.



common to both methods. The method with DMAI also uses DMF as a solvent, “toxic for reproduction” (CLH) and included in “the candidate list of substances of very high concern” (SVHC); toluene, “suspected to be toxic for reproduction” (CLH); and TOPO, “most of the data submitters agree that this substance is a skin sensitizer” (CLP). In the Ni(AcO)₂ method, these three substances are not employed. Instead, a new substance with properties of concern, Ni(AcO)₂·4H₂O, is added, “most data submitters agree that this substance is a skin sensitizer and a respiratory sensitizer” (CLP).

Conclusions

Our synthetic approach is designed to offer a rapid-crystallization (<10 s), DMAI/HI-free approach, and a more environmentally friendly (antisolvent and DMF-free) synthesis method to enhance the stability and performance of γ -CsPbI₃-Ni(AcO)₂ PSCs. Employing this approach, our champion device, incorporating a 7.7% mol of Ni(AcO)₂, exhibits a PCE exceeding 12% in a n-i-p mesoscopic configuration with a lifetime of >600 h at MPP with minimum losses (<20%). The tests performed under low-intensity illumination (cool and warm white illuminations) exhibit promising efficiencies over 15 and 17%, highlighting the potential of CsPbI₃-Ni(AcO)₂ PSCs for efficient energy harvesting in low-intensity illumination environments. Moreover, the new synthesis method with Ni(AcO)₂ reduces by 70% the GW and most of the impact categories. The addition of Ni(AcO)₂, potentially harmful for skin and respiratory sensitizing, has a low impact on human toxicity categories, which are highly affected by lead iodide. In addition, our DMSO-only method avoids the use of different substances with properties of concern, such as DMF, toluene, and TOPO. Nevertheless, these improvements should be viewed with caution, as substances of concern (Ni(AcO)₂ and PbI₂) persist in the absorbing layer.

We believe that our straightforward, DMSO-only, DMAI/HI-free and antisolvent-free synthetic approach paves the way for the development of highly efficient and stable all-inorganic perovskite materials for photovoltaics.

Experimental section

Chemicals

CsI (99.999%, Sigma-Aldrich), lead(II) iodide (PbI₂, 99.99%, TCI), dimethyl sulfoxide (DMSO, 99.9%, Sigma-Aldrich), isopropanol (IPA, 98%, Avantor), chlorobenzene (99.8%, Sigma-Aldrich), tris(2-(1*H*-pyrazol-1-yl)-4-*tert*-butylpyridine)cobalt(III) tri[bis(trifluoromethane) sulfonimide] (FK209, Sigma Aldrich), 30 NR-D transparent titania paste (GreatCell Solar Materials), bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI, Sigma-Aldrich), ethanol (99.9%, Merck), spiro-OMeTAD (Lumtec), titanium diisopropoxide bis(acetylacetonate) (TIAP, 75 wt% in isopropanol, Sigma-Aldrich), 4-*tert*-butyl pyridine (tBP 98%, Sigma-Aldrich), nickel(II) acetate tetrahydrate (Ni(AcO)₂·4H₂O, 99% Thermo Scientific Chemicals). All chemicals are used as received.

FTO substrates cleaning

Unpatterned FTO substrates are used (TEC 15, Ossila, with dimensions 2 cm × 1.5 cm). Substrates are cleaned with 2% Extran solution with a very fine brush to clean the FTO surface, then washed with distilled water to remove soap contents. Afterwards cleaned with ethanol, acetone and isopropanol for 15 min by sonication. After drying with a nitrogen gun, the substrates are placed in a UV-ozone cleaner for 15 minutes right before the titanium oxide layer deposition.

Solution preparation

2% Extran solution is made by mixing 20 mL in 1000 mL distilled water.

TiO₂ solution is prepared by adding 1000 μ L TIAP into 9 mL of ethanol.

1.5 M CsI solution is prepared by dissolving 1.063 g of CsI solution in 2.726 mL DMSO solvent. The mixture is stirred 30 minutes until complete solubilization of CsI to get the solution.

To get 1.3 M CsPbI₃ solution, 2.274 mL CsI solution is added in 1.145 g PbI₂ salt and stirred for 30 min at 80 °C until it completely dissolved.

To make 1.3 : 0.1 (molar ratio) CsPbI₃ : Ni(AcO)₂ solution, 1 mL above CsPbI₃ solution is added to 0.025 g of Ni(AcO)₂ and stirred for 30 min until a clear, green-yellowish perovskite solution is formed.

A 70 mM solution of spiro-OMeTAD is prepared by dissolving 90 mg spiro-OMeTAD in 982.26 μ L chlorobenzene with 35.5 μ L tBP, 20.40 μ L LiTFSI with a stock solution of 520 mg mL⁻¹ in acetonitrile, and 22.22 μ L FK209 with a stock solution of 375 mg mL⁻¹ in acetonitrile.

Device fabrication

TiO₂ compact layer. TiO₂ compact layer is deposited by spray pyrolysis with oxygen as the carrier gas. One edge of each substrate is covered by around 5 mm using a guided-metal holder containing the substrates of conductive FTO to avoid the side being exposed. Then the substrates are heated up to 450 °C and are kept at this temperature for 15 min before and 30 min after the spray of the precursor solution. The whole solution is transferred into a spray nozzle and sprayed at roughly 25 cm away from the substrates with an inclination angle of 45°, with at least 20 seconds of delay between each spraying cycle. Afterward, substrates are left to cool down to room temperature and then put in an ozone chamber for 15 minutes before perovskite film deposition.

TiO₂ mesoscopic layer. TiO₂ compact layer is deposited by spin coating. The as-prepared TiO₂ compact layers are coated using 70 mL of 30-NRD titania paste solution (150 mg mL⁻¹ in Ethanol). The spinning time is set at 20 s at 4000 rpm. Following the deposition step the substrates are annealed all at once starting from 100 °C as sequentially deposited and then heated up to 450 °C for 30 min.

Deposition of perovskite films. Substrates are transferred into a glove box filled with nitrogen (O₂ < 0.1 ppm, H₂O < 0.1 ppm). The substrates are placed on a hot plate at 100 °C for



5 min before perovskite deposition. 50 μL perovskite solution is added and spin-coated quickly at 4000 rpm for 40 seconds. The wet films are then annealed at 75 $^{\circ}\text{C}$ for roughly 10 s and then transferred to a different hot plate at 200 $^{\circ}\text{C}$ for a 10 s fast crystallization.

Hole transport layer deposition. 50 μL spiro-OMeTAD solution is dynamic-deposited by spin coating at 4000 rpm for 30 seconds accelerating at 800 rpm s^{-1} depositing the solution after 3 s starting the program. Afterward, all the samples are transferred into a dry air box (relative humidity (RH) < 20%) for oxygen soaking.

Deposition of metal contact. Gold is evaporated using a thermal evaporator under a vacuum of approximately 10^{-6} mbar. The deposition rate is programmed at 0.02 \AA s^{-1} for the first 1 nm, 0.1–0.2 \AA s^{-1} for the following 5 nm, then 0.5 \AA s^{-1} until 20 nm and then 1 \AA s^{-1} for the rest of the deposition. Overall, it takes around 25 min for the deposition of 80 nm of gold.

Structural and optical characterization. Morphological analysis is conducted using a HITACHI S-4800 field-emission scanning electron microscope (SEM) operating at 20 kV. Crystalline structure is determined by X-ray diffraction (XRD) using a PANalytical Empyrean X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{\AA}$), covering a Bragg angle range of 4–60 $^{\circ}$ with a step size of 0.026 $^{\circ}$. UV-visible (UV-vis) measurements are conducted using a Shimadzu UV-2501PC spectrophotometer. All PL spectra are obtained with a CW GaN laser (404 nm). Photoluminescence (PL) characterization is conducted using an Edinburgh Instruments FLS 1000 spectrometer equipped with a double-grating Czerny–Turner monochromator for excitation and detection. The detection system, featuring a high-speed photomultiplier tube (PMT) in a cooled housing, is used to record both steady-state PL Spectra. XPS measurements are performed in a Thermo Scientific K-alpha X-ray photoelectron spectrometer system (based pressure 4×10^{-9} mbar). Photoelectrons are excited with Al $K\alpha$ line 1486.6 eV of a monochromatized X-ray source. Measurements are taken at room temperature with a pass energy of 20 eV, with a spot size 400 μm .

Electrical characterization. J - V curve measurements are conducted under ambient conditions using an Ossila class AAA solar simulator and an automated J - V measurement system (T2003B3-G2009A1). The light intensity was calibrated to 1 sun (100 mW cm^{-2}) with a certified Si solar cell (RERA Solutions, RQN3290, RQN001). Measurements are performed without encapsulation at an ambient temperature of $\sim 25 \text{ }^{\circ}\text{C}$ and RH < 10%, with an active device area of 0.026 cm^2 defined by a mask.

The MPP of the solar cells is evaluated under nitrogen (N_2) atmosphere. The stability protocol involved measuring an initial J - V curve to determine the maximum power point voltage (V_{max}), which is then applied to the cell for 1 hour under continuous illumination. After each hour, a new J - V curve is recorded to update the V_{max} , which is subsequently applied for the next hour. Solar cell parameters are monitored and recorded after each J - V measurement throughout the MPP. Enhanced low-intensity illuminations are obtained using the same Ossila

class AAA solar simulator selecting the “cool white” and “warm white” LEDs from the software.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

The data supporting the findings of this study are available from the corresponding author upon request. Supplementary information is available, see DOI: <https://doi.org/10.1039/d5el00064e>.

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