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# Printed CsMg–ZnO ETLs achieve over 9 % efficiency in PbS quantum dot solar cells

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# ABSTRACT

Zinc oxide (ZnO) is a key electron transport layer (ETL) material in next-generation lead sulfide (PbS) colloidal quantum dot solar cells (CQDSCs) due to its high transparency, strong exciton binding energy, and good electron mobility. Here, we demonstrate a scalable doctor-blading printing protocol for ZnO ETLs that integrates dual defect passivation with magnesium ( $Mg^{2*}$ ) and caesium ( $Cs^*$ ) and employs solvent engineering to achieve uniform, defect-minimized films. Using a ternary solvent blend (methanol, chloroform, and 2-methoxyethanol) optimizes the ink's viscosity and boiling point, preventing particle migration and ensuring full substrate coverage. Our modified ZnO ink leads to improved crystallinity, smoother surfaces, and reduced trap states, boosting the fill factor (FF) and short-circuit current ( $J_{sc}$ ). Consequently, we achieve a power conversion efficiency increase from 5.98 % to 9.53 % using a printed CsMg-ZnO film. Notably, 80 % of dual-doped devices exceeded 7.5 % efficiency, demonstrating high reproducibility and reliability. This performance enhancement underscores the effectiveness of dual metal ion treatment and solvent engineering strategies in overcoming printability challenges. Moreover, the compatibility of our approach with low-temperature processing and established coating techniques paves the way for seamless integration into large-scale manufacturing, bringing PbS CQDSCs closer to commercial viability.

#### 1. Introduction

Colloidal quantum dot (CQD) solar cells based on PbS have emerged as a promising platform for next-generation photovoltaics, offering sizetunable absorption, compatibility with low-cost solution processing, and high potential for large-scale production [1,2]. A watershed moment in their development came with the introduction of solution-phase ligand exchange (SPLE) methods, enabling the formation of high-quality CQD inks and simplifying device fabrication [1-3]. These advances have propelled single-junction PbS CQD solar cells to record power conversion efficiencies (PCEs) exceeding 15 % through lab-scale techniques such as spin coating and vapor deposition [3-9]. As the field approaches commercial viability, scalable processing methods, including roll-to-roll (R2R) and inkjet printing, become crucial for industrial deployment [2, 5]. Among the key components of state-of-the-art PbS CQD photovoltaics is the ETL, where ZnO stands out for its high transparency, strong exciton binding energy, and excellent electron mobility [10-12]. ZnO films prepared via hydrolysis-condensation (HC-ZnO) methods have

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demonstrated smoother surfaces, fewer crystal defects, and superior charge transport compared to sol-gel derived films and is used in today's state-of-the-art PbS-CQDSCs [3,6-8,10,13]. However, despite these intrinsic advantages, conventional spin-coating strategies are not easily transferable to large-area manufacturing due to material waste and limited throughput [3,5-8,14]. Doctor blade coating—a meniscus-controlled printing technique-has shown promise for scalable COD absorber layers and hole transport layers (HTLs) [14–19], but achieving uniform, defect-minimized ZnO ETLs suitable for high-performance CQD devices using this method remains a challenge. Recent studies have shown that defect passivation can improve the quality of ETLs in solar cells [20-27]. Incorporating heteroatoms such as sodium, potassium, indium, magnesium, and caesium into ZnO films has been found to reduce oxygen vacancies, suppress trap states, and enhance charge extraction and overall device performance [13,20-27]. For example, magnesium doping improves crystallinity and reduces defect density [23,24], while caesium doping can enhance surface roughness and energy-level alignment at the ETL/absorber interface [26,27]. Yet, while these doping strategies are well-documented for spin-coated ZnO layers, their integration into scalable printing processes remains largely unexplored. Currently, solvents like methanol (MeOH) and chloroform (CHCl<sub>3</sub>) are commonly used for HC-ZnO CQDs, as they provide short-term stability due to their favourable polarity [28,29]. The low boiling points ( $T_{MeOH} = 65 \degree C$ ,  $T_{CHCI3} = 61 \degree C$ ) [30,31], vapor pressure, and viscosity of these solvents are well-suited for spin coating, where inks are dispersed by centrifugal force. However, replicating this process in scalable printing technologies, such as doctor blade coating or roll-to-roll manufacturing, is challenging. The slower drying process inherent to doctor blade coating, compared to spin coating, necessitates modifications in ink composition and solvent selection [32-34]. In this work, we demonstrate the first doctor-blade-based printing protocol for ZnO ETLs in PbS CQD solar cells by synergistically combining dual defect passivation (Mg $^{2_{+}}$  and Cs $^{+}$  co-doping) with a solvent engineering strategy. By leveraging a ternary solvent mixture (methanol, chloroform, and 2-methoxyethanol) to balance volatility, viscosity, and polarity, we achieve uniform, colloidally stable ZnO inks that form smooth, defect-passivated ETLs under meniscus-controlled deposition. This approach not only improves the film's crystallinity, carrier mobility, and morphological homogeneity but also boosts the fill FF and Jsc, culminating in a PCE improvement from 5.98 % to 9.53 %. Importantly, our method demonstrates high reproducibility, with 80 % of dual metal ion treated devices achieving efficiencies exceeding 7.5 %, highlighting its reliability and potential for large-scale manufacturing. Our findings highlight the power of integrating dual metal ion treatments with tailored ink formulations to overcome longstanding printability challenges. More broadly, this work provides a scalable route toward fully printed, cost-effective CQD photovoltaics, bringing us one step closer to the commercialization of high-performance CQD solar modules.

# 2. Experimental section

# 2.1. Materials

Acetonitrile (ACN, Sigma-Aldrich, 99.9 %), butylamine (BTA, Sigma-Aldrich, 99.5 %), dimethylformamide (DMF, anhydrous, Sigma-Aldrich, 99.8 %), 1,2-ethanedithiol (EDT, anhydrous, Sigma-Aldrich, synthesis grade), potassium hydroxide (KOH, Merck for analysis), oleic acid (OA, Sigma-Aldrich 90 %, technical grade), octane (Sigma-Aldrich 98 %, reagent grade), 1-octadecene (ODE, Sigma-Aldrich, synthesis grade), lead bromide (PbBr2, Sigma-Aldrich, 99.999 %), lead iodide (PbI2, TCI 99.999 %), lead(II) oxide (PbO, Sigma-Aldrich, 99.999 %), bis(trimethylsilyl)sulfid (TMS, Sigma-Aldrich, synthesis grade), toluene (anhydrous, Sigma-Aldrich, 99.8 %), zinc acetate dihydrate (Zn(CH3COO)<sub>2</sub> × 2H<sub>2</sub>O, Sigma-Aldrich, 99.5 %), 2-methoxyethanol (2-ME, Sigma-Aldrich, anhydrous, 99.8 %), chloroform (Sigma-Aldrich, 99 %), methanol (Sigma-Aldrich, 99.7 %), acetone (Sigma-Aldrich, 99.8 %), caesium chloride (CsCl, Sigma-Aldrich 99.999 %), magnesium acetate tetrahydrate (Sigma-Aldrich, 99 %).

# 2.2. ZnO nanocrystal (NC) synthesis

The preparation of pure ZnO in the form of colloidal nanoparticles was as follows: Zinc acetate dihydrate (1.590 g, 7.24 mmol) was first dissolved in methanol (85 mL) under constant stirring at 63 °C. Subsequently, a solution of potassium hydroxide (0.800 g, 16 mmol) in methanol (16 mL) was added within 10 min to the zinc acetate dihydrate solution. For sedimentation, the solution was removed from the hot plate after 3h and stored for 12 h at room temperature. In the next step, the supernatant was removed, and the precipitate was redispersed with methanol (37.5 mL) and centrifuged (3 min, 2500 rpm). In the second wash, the material was again dissolved in methanol (37.5 mL) and centrifuged (3 min, 5500 rpm). Subsequently, the supernatant was discarded, and the product was dried under vacuum. For nano ink preparation, the QDs were redispersed in a mixture of chloroform and methanol in a 1:1 ratio.

For the preparation of Cs- and Mg-treated ZnO, the synthesis procedure for pristine ZnO as described above was extended by placing either CsCl (61 mg, 5 mol-%) or Mg(Ac)2•4H2O (78 mg, 5 mol-%) as a second precursor together with zinc acetate dihydrate to the reaction flask before adding the KOH solution. The synthesis procedure and the purification step were similar as for the preparation of the pristine ZnO powder.

Preparation of modified ZnO nano inks: For the preparation of Csand Mg-treated nano inks, Cs-ZnO and Mg-ZnO powders were dissolved in 1:1 mixture of Chloroform:MeOH separately and then diluted in 2-ME to obtain a final ZnO concentration of 100 mg/mL. For the fabrication of the CsMg-ZnO nano ink both inks were mixed in a volume-ratio of 1:1 and vortexed for 1 min.

#### 2.3. Preparation of PbS quantum dots (QDs)

PbS quantum dots were synthetized via the hot-injection method. Lead (II) oxide (900 mg, 4 mmol) together with oleic acid (2732 g) was dissolved in 1-octadecene (52.5 mL) under inert gas atmosphere. The solution was degassed for 1 h under vacuum at 150  $^\circ\mathrm{C}$  to form the lead oleate precursor. The temperature was decreased to 100  $^\circ\text{C}$  (T\_{Inj}) and bis (trimethylsilyl)sulfid (420 µL, 2 mmol) dissolved in 1-octadecene (5 mL) was injected rapidly under nitrogen atmosphere to start the nanocrystal formation process. The solution immediately changed from clear yellow to dark black and was quenched in an ice bath after a reaction time (t<sub>reaction</sub>) of 5 min. The solution was loaded into four centrifuge tubes and the nanoparticles were precipitated upon addition of a 1:1 mixture of ethanol and acetone (15 mL). After centrifugation (10 min, 7830 rpm), the supernatant was discarded and the nanoparticles were washed two times by redispersion in octane (7.5 mL) followed by precipitation with acetone and ethanol (15 mL). After centrifugation (10 min, 7830 rpm) and removal of the supernatant, the nanoparticles were dried in vacuum for 10 min and redispersed octane (50 mg/mL) before film deposition. Smaller PbS quantum dots synthesized with a slightly different recipe (PbO = 2 mmol; ODE = 23.77 mL, OA = 900 mg, TMS = 210  $\mu$ L in 5 mL ODE) and process parameters (T<sub>Inj</sub> (TMS) = 85 °C,  $t_{reaction} = 1$  min) were used for the HTL.

#### 2.4. Preparation of the PbS nano inks

A solution of lead iodide (2 mmol), lead bromide (0.4 mmol) and ammonium acetate (1.1 mmol) in DMF (20 mL) and a solution of lead sulfide nanocrystals (140 mg) in octane (20 mL) were prepared. Both solutions were transferred into a centrifuge tube via a 0.45  $\mu$ m PETfilter. The mixture was vortexed for 3 min and the clear octane phase was carefully removed. The remaining DMF phase was washed three times by addition of octane (10 mL), vortexing for 3 min and disposal of the octane phase. The ligand exchanged nanocrystals were then precipitated with 11 mL of toluene. The clear and yellow supernatant was discarded after centrifugation (10 min, 7830 rpm), the tube inside walls were cleaned with a cotton stick and the nanocrystals were dried in vacuum. Finally, the nanocrystals were redispersed in butylamine (300 mg/mL) and used for spin-coating.

#### 2.5. Fabrication of PbS-based solar cells

The substrates for device fabrication were prepared from ITO covered glass (KINTEC, 15  $\Omega$ /sq) of 3 cm  $\times$  3 cm size and were patterned by etching the desired areas with zinc powder and 3M hydrochloric acid, polished with detergent and then subsequently ultrasonicated with deionized water, acetone and isopropanol for 15 min each. The substrates were exposed to O2-Plasma for 20 min to remove organic residues from the surface immediately before ZnO fabrication. The electron transport layer was fabricated using the doctor blade coating technology (Zehntner ZAA 2300 automatic film applicator). 70 µL of pristine or modified ZnO solution (100 mg/mL) were deposited on the substrate and blade coated with a speed of 40 mm/s, the slit size was set to  $170 \,\mu m$ and the film deposition was carried out at room temperature. For the following steps, the substrates were transferred into a nitrogen filled glovebox. For the active layer, 80 µL of ligand exchanged lead sulfide nanocrystals with an absorption wavelength of 950 nm dissolved in butylamine (300 mg/mL) were deposited on the substrate before spincoating at 2500 rpm for 30 s. The substrates were then annealed at 80 °C for 10 min. For the hole transport layer, 70 µL of oleic acid-capped lead sulfide nanocrystals with an absorption wavelength of 850 nm dissolved in octane (50 mg/mL) were deposited on the substrates followed by spin-coating at 2500 rpm for 30 s. For ligand exchange, the whole film was then covered with a solution of 0.01 vol.-% of EDT in acetonitrile for 30 s followed by spin-coating at 2500 rpm for 30 s. The film was then covered with 450  $\mu L$  acetonitrile and spin coated at 2500 rpm for 30 s (3 runs). This procedure was repeated for a second HTL. The material at the edges of the substrates was removed with a razor blade to enable to contact the bottom ITO electrode before thermal evaporation of 40 nm of gold for the back contacts.

#### 2.6. Characterization

# 2.6.1. Morphological and dimensional characterization

Dynamic light scattering (DLS): was performed in quartz cuvettes on a Zetasizer Nano-ZS from Malvern Instruments. A He/Ne-laser with a wavelength of 632.28 nm was used, and the scattering angle was set to  $90^{\circ}$ .

Scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX): were conducted using a Fisher-Scientific Dual Beam Helios Nanolab G3 UC microscope. Cross-sectional and top-view images, as well as EDX studies, were performed at acceleration voltages of 5 kV and 2 kV, respectively. Prior to imaging, carbon sputtering was applied to all samples, and both mirror and through the lens detectors were utilized.

Transmission electron microscopy (TEM): High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was performed using a probe-corrected FEI Titan Themis 60-300 TEM operated at 300 keV. The sample material was drop-casted onto Quantifoil® copper grids with an amorphous carbon film thickness of 2 nm.

Atomic force microscopy (AFM): The AFM measurements were carried with the help of atomic force microscope mode in NeaSNOM instrument from attocube systems AG. Gold tips (TAP190G-GB) were used in intermittent contact mode at a resonant frequency (R.F.  $\sim$  160 kHz) and at a tapping amplitude of 80 nm. Gwyddion software was used for processing the images. The topography images shown were flattened by plane subtraction and background polynomial removal.

#### 2.6.2. Optical and structural analysis

UV–Vis-Absorption spectroscopy: Absorption measurements were conducted using a PerkinElmer Lambda 1050 UV/Vis/IR absorption spectrophotometer, which was equipped with a 150 mm integration sphere. Nano dispersions and thin films were analysed in absorbance mode.

Photoluminescence spectroscopy (PL): PL measurements were conducted in an ambient air environment using a FluoTime 300 spectro-fluorometer by PicoQuant GmbH. For steady-state measurements, we used a pulsed solid-state laser operating at a 375 nm wavelength (LDH375 from PicoQuant) at a repetition rate of 40 MHz, with a fluence of 20 pJ/cm<sup>2</sup> to establish and maintain steady-state conditions.

Powder x-ray diffraction (P-XRD): P-XRD analysis utilized a Stoe Stadi P diffractometer in Debye–Scherrer geometry, operating at 40 kV and 40 mA. The system employed monochromatic Cu-K $\alpha$ 1 radiation ( $\lambda$  = 1.5406 Å) through a Ge(111) single crystal monochromator. Detection was facilitated by a Dectris Mythen 1k detector. Sample materials for measurement were positioned between slim, transparent foils, secured within a flat, circular holder. The acquisition of all XRD patterns was carried out at ambient room temperature.

#### 2.6.3. Device performance measurements

Current–Voltage (J-V) characterization: J-V measurements of the CQDSC devices were conducted using a Newport Oriel Sol 2A solar simulator along with a Keithley 2401 source meter. The devices were subjected to illumination through a shadow mask, resulting in an active area of  $0.0831 \text{ cm}^2$ . The J-V curves were generated under standard AM 1.5G solar illumination using a xenon lamp and were calibrated to a light intensity of 100 mW/cm<sup>2</sup> using a silicon diode certified by Fraunhofer ISE.

External quantum efficiency (EQE): The EQE was taken by subjecting the cells to monochromatic illumination (170 W halogen lamp on a Bentham Instruments power supply passing through a Quantum Design MSH 300 monochromator). The light was chopped at a frequency of 100 Hz and the signal was amplified by a Stanford Research Systems SR830 Lock-In amplifier. The calibration was performed using a calibrated silicon photodiode and a germanium sensor.

# 2.6.4. Compositional and electronic structure

X-ray photoelectron spectroscopy (XPS): XPS measurements were performed with a VSW TA10 X-ray source providing non-monochromatized Al-K $\alpha$  radiation and using a VSW HA100 hemispherical analyser. All samples were prepared in N<sub>2</sub>-filled glovebox and measured directly after fabrication. The x-ray source was operated at 15 mA and 12 kV. The pass energy was set to 22 eV and the dwell time was set at 0.1 s per measurement point for all recorded core spectra and 1.0 s for the survey spectrum. The system was calibrated on the binding energies of Au 4f7/2, Ag 3d5/2, and Cu 2p3/2.

Ultraviolet photoelectron spectroscopy (UPS): The samples were sealed in a nitrogen atmosphere and delivered to Darmstadt, where they were opened in a glovebox filled with N2, and then transferred under vacuum to the DAISY-SOL lab's cluster tool. UPS measurements were performed with a Thermo Fisher VG Escalab 250 spectrometer with He I (h $\nu = 21.2$  eV) as a UV source, with a fixed He pressure of 2.5  $\times$   $10^{-8}$ mbar. The machine has been calibrated by using Ar-sputtered Ag, Au, and Cu foils. The Fermi level of the cleaned silver was also used to determine an instrumental resolution of 0.24 eV for UPS (pass energy of 2.5 eV). UPS spectra were acquired with a step size of 0.05 eV, a dwell time of 50 ms and a pass energy of 2.5 eV. A bias of 6 V or 8 V has been applied to the sample to determine the energy cut-off and corrected while plotting the spectra. The absolute position of the VBM was determined using the derivatives method described and applied to TiO<sub>2</sub> in Ref. [35]; it consists in using the 1st and the 2nd derivative of the UPS spectra to detect the very first photoelectrons with the lowest binding energy. Indeed, the standard linear extrapolation method, which consists in taking the intersection between two linear extrapolations, gives

an energy difference between the Fermi level and the VBM higher than the optical band gap (e.g., 3.54 eV for pristine ZnO) and would result in a Fermi level inside the conduction band.

#### 3. Results and discussion

In the first step of ink fabrication, Mg-ZnO and Cs-ZnO nanoparticles treated with 5 mol-% were synthesized using a modified solutionprocessed ZnO protocol (see Fig. 1) [12]. In brief, zinc acetate (ZnAc), along with magnesium acetate (MgAc) or caesium chloride (CsCl), was placed in a reaction flask and dissolved in methanol (MeOH) at 63 °C. After the precursor materials were dissolved, potassium hydroxide (KOH) dispersed in methanol was added drop by drop, followed by a heating step at 63 °C for 3 h (see experimental section for details). Differences in reaction kinetics were observed during the hydrolysis-condensation process compared to pristine ZnO used as the control. The onset of Zn(OH)<sub>2</sub> intermediate formation through the hydrolysis reaction was indicated by a temporary clouding of the initially transparent precursor solution. This phenomenon was observed in the synthesis of Mg- and Cs-treated ZnO, occurring 9 min and 6 min earlier, respectively, before the turbidity appeared in the control. Similar results were observed during the second step of ZnO synthesis involving the condensation reaction. Clearly, the addition of metal ions accelerated the formation of the final ZnO, as evidenced by the earlier clouding in the reaction solutions containing Cs and Mg. These differences in reaction kinetics indicate a impact on the formation and growth of nanocrystals, leading to different sizes and size distributions. A TEM analysis revealed that the metal ion treatment has a considerable impact on the resulting ZnO crystal size. A trend toward larger sizes with the average crystal diameters of 4.6 nm, 5.1 nm and 6.6 nm was observed for pristine ZnO, Cs-ZnO and Mg-ZnO, respectively which is consistent with XRD and DLS measurements (see Fig. 1a-b, Fig. S1-1, S2). The resulting Mg-ZnO and Cs-ZnO dispersions were washed in fresh MeOH for further fabrication. For the nano ink preparation, the purified ZnO nanocrystals were vacuum dried and dissolved in a binary solvent system consisting of a 1:1 ratio (vol.-%) of CHCl<sub>3</sub> and MeOH. To design a printing protocol adaptable for the doctor blading process a solvent engineering strategy was implemented which improved the drying-behaviour of the nano ink (see Fig. 1). In particular, this approach enabled the fabrication of devices with good reproducibility. Optimal printing properties for the doctor blade technology were achieved by using a ternary solvent system consisting of CHCl<sub>3</sub>, MeOH, and 2-ME in a 1:1:1 ratio (vol.-%). This specific composition offers a balance of key attributes. CHCl<sub>3</sub> and MeOH, with their appropriate polarity, maintain the stability of nanoparticles in the solution. However, the high vapor pressure of these solvents (see Fig. 1c) makes them excessively volatile which results in a high film drying rate. Consequently, this characteristic renders them inappropriate for the slow film drying process associated with meniscus-controlled doctor blading. To overcome this solvent volatility challenge, the introduction of a third component became essential. The addition of 2-ME (T<sub>boil</sub> = 125  $^{\circ}$ C, P<sub>vap</sub> = 10 hPa) increased the boiling point and reduced the vapor pressure of the ternary solvent system. The slower evaporation of the solvents could ensure complete wetting of the substrate and effectively avoid the formation of inhomogeneous crystal growth during the film drying process. In addition, the viscosity and surface tension of the solvent system could be optimally matched to the printing process, resulting in a well-distributed, full-covered CsMg-ZnO ink over the desired printing area (see Fig. 1d). The performance of CsMg-ZnO as an ETL for PbS-based CQD solar cells was investigated by using a standard device architecture consisting of a transparent indium tin oxide (ITO) front electrode, a thin ZnO film as the ETL, a photoactive layer of lead halide-capped PbS QDs, an EDT-capped PbS QD film as the HTL, and a thin Au layer as the back

electrode (see Fig. 2a). Solar cells with CsMg-ZnO, Cs-ZnO, or Mg-ZnO ETLs were fabricated along with pristine ZnO as a control device. The cross-section of the devices was investigated with scanning electron microscopy (SEM) to determine the thickness of each layer. An SEM image of the CsMg-champion device based on a blade coated ZnO-ETL is depicted in Fig. 2b, with a corresponding average layer thickness of approximately 127 nm  $\pm$  2.59, 118 nm  $\pm$  4.09, 274 nm  $\pm$  3.66, and 48



**Fig. 1.** Fabrication procedure of the CsMg-ZnO nano ink designed for the doctor blade coating technology. *Step (I):* Synthesis route of Mg- and Cs-treated ZnO-QDs with the corresponding HAADF-STEM image showing (a) 5 mol-% Cs-ZnO and (b) 5%-mol Mg-ZnO with a particle diameter of around 5.1 nm and 6.6 nm, respectively. *Step (II):* Nano ink fabrication procedure for the synthesis of the printable CsMg-ZnO ink made of a ternary solvent system (1:1:1 vol.-% mixture of CHCl<sub>3</sub>:MeOH:2-ME (2-methoxyethanol)). (c) A solvent properties table demonstrating the optimization of the following physical ink properties: boiling point, vapor pressure, polarity, and viscosity. *Step (II):* Illustration of the blade coating process for the CsMg-ZnO ETL and (d) an image of a blade coated CsMg-ZnO ETL on an ITO-substrate, demonstrating the notably uniform film formation obtained through implementation of the ternary solvent system.



**Fig. 2.** (a) Schematic of the PbS-CQDSC device architecture, accompanied by (b) the corresponding SEM cross-section images (left: backscattered electron analysis, right: secondary electron analysis). (c) Comparison of solar cell performance across different ZnO ETL types — pristine ZnO, Mg-ZnO, Cs-ZnO, and CsMg-ZnO — using the complete set of PbS devices. (d) Averaged J-V curves for the 10 PbS-CQDSC devices with the highest efficiencies for each ZnO-ETL type, all exceeding the 2.5 % PCE threshold level. All devices were fabricated using ZnO nano inks according to the procedure detailed in Fig. 1, with a modified ternary solvent system.

nm  $\pm$  4.77 for ITO, CsMg-ZnO, PbS-PbI<sub>2</sub> + PbS-EDT and Au, respectively (the corresponding device performance data can be found in the SI, Fig. S3a). In Fig. 2c, the comprehensive performance evaluation of the entire set of PbS devices is highlighted, revealing two benefits across the modified ZnO configurations: Elevated PCE and enhanced reproducibility. Notably, CsMg-ZnO emerges as the top-performing variant in both aspects, as detailed in Fig. 2c and Table 1 (the corresponding box plot diagrams representing Jsc and Voc data can be found in Fig. S3b).

The optimized reproducibility is evident from the narrow distribution of key parameters, including FF,  $J_{sc}$ , and  $V_{oc}$ . Consequently, CsMg-ZnO attains the highest average efficiency (PCE<sub>mean</sub> = 8.4 %) with a minimal standard deviation (STD) of  $\pm 0.85$ . As illustrated in Fig. 3, 80 % of the CsMg-ZnO devices achieved a PCE exceeding 7.5 %, while only 35 % of Cs-ZnO, 25 % of Mg-ZnO, and none of the pristine ZnO devices reached this efficiency. Fig. 2d displays the average current density/ voltage (J-V) characteristics of the ten most-efficient devices for each ZnO type, measured under AM 1.5G illumination. The analysis confirms that the efficiency enhancements are primarily driven by an increase in FF, particularly in CsMg-ZnO-based devices, which also contribute to the observed enhancements in  $J_{sc}$ . The improved external quantum efficiency (EQE) in metal-treated PbS-CQD devices is consistent with these findings (for details see SI fig. S4, S5 and Table S1). To further investigate these improvements in  $J_{sc}$  and FF, conductivity measurements were

#### Table 1

Optimized photovoltaic parameters of PbS-CQD devices based on different metal ion treatments (mean values are based on 20 different devices of each solar cell type).

ETL	Voc <sub>mean</sub> [V]	Jsc <sub>mean</sub> [mA/cm <sup>2</sup> ]	FF <sub>mean</sub> [%]	PCEmean [%]
CsMg-ZnO Cs-ZnO Mg-ZnO Pristine ZnO	$\begin{array}{c} 0.61 \pm 0.01 \\ 0.60 \pm 0.02 \\ 0.53 \pm 0.17 \\ 0.42 \pm 0.29 \end{array}$	$\begin{array}{c} 23.25 \pm 1.62 \\ 22.82 \pm 3.41 \\ 20.36 \pm 5.31 \\ 15.36 \pm 7.07 \end{array}$	$\begin{array}{c} 57.8 \pm 5.32 \\ 49.1 \pm 10.11 \\ 43.9 \pm 12.90 \\ 32.3 \pm 7.10 \end{array}$	$egin{array}{c} 8.4 \pm 0.85 \\ 6.9 \pm 1.84 \\ 5.5 \pm 2.76 \\ 2.8 \pm 2.35 \end{array}$



**Fig. 3.** Illustration of the reproducibility improvement in PbS-CQDSCs with different ZnO-ETL types, shown in three categories: number of devices with efficiencies  $\geq$ 7.5 % (a),  $\geq$ 5 % (b), and  $\geq$ 2.5 % (c) across all solar cells.

performed on ETL-only devices (see Fig. 4a). The results show a similar trend to the solar cells performance with increased conductivity for all modified ZnO interface layers. The electrical conductivity ( $\sigma$ ) was determined using the formula  $\sigma = I/V \ge A/d$ , where I is the current, V is the voltage, A is the device area and d represents the thickness of the film. [25, 36, 37] The conductivities of pristine ZnO, Mg-ZnO, Cs-ZnO and CsMg-ZnO films were calculated to be  $3.78 \times 10^{-6}$ ,  $7.15 \times 10^{-6}$ ,  $1.37 \times 10^{-5}$ ,  $2.36 \times 10^{-5}$  S/m, respectively (see Fig. S6). To study the influence of the metal ion treatment on the crystal structure of ZnO, X-ray diffraction (XRD) measurements were performed. The characteristic reflections of the ZnO crystal structure were observed, confirming the hexagonal wurtzite phase (JCPDS card no. 36–1451) in all samples [38]. The three main reflections (100), (002), and (101) are shown in



Fig. 4. (a) J/V-curves of ETL-only devices made of pristine ZnO, Cs-ZnO, Mg-ZnO and CsMg-ZnO thin films (architecture: Glass/ZnO-ETL/Au). The corresponding (b) XRD data, (c) PL-spectra and (d) Transmission spectra.

Fig. 4b. To identify the lattice parameters and crystal sizes, Rietveld refinements were performed (Figs. S1-1), confirming the P63mc ZnO phase and average crystallite sizes of 5.9 nm for pristine ZnO, 8.1 nm for Cs-ZnO, 18.2 nm for Mg-ZnO and 9.8 nm for CsMg-ZnO. These results are, in good agreement with the TEM and DLS results (Fig. 1a-b, Fig. S2). Rietveld refinements also revealed a small amount of a side fraction in this ZnO batch (for details see SI, fig. S1-1, S1-2, S1-3). All modified ZnO samples exhibit enhanced crystallinity, evidenced by reduced full-width at half maximum (FWHM) and increased crystallite size. This improvement aligns with well-documented effects of ZnO treatments with metal ions such as Mg and Cs [24,25]. Literature reports indicate that these treatments mitigate oxygen vacancies and other defect sites, thereby lowering trap densities and reducing recombination losses [20–25]. By creating a more ordered lattice and mitigating defect states, Mg and Cs treatments improve both electron mobility and carrier lifetime. This reduction in defect density is further corroborated by the diminished defect-related PL emission and the shifts in the O 1s XPS signals observed in our samples, aligning with prior findings on doped ZnO materials [22,24,25]. As a direct result, the Cs and Mg treated ZnO ETLs enable more efficient charge extraction, enhancing Jsc, FF, and the overall PCE of our devices. These improvements leverage the inherent advantages of the hydrolysis-condensation (HC) approach. Unlike sol-gel (SG) ZnO, which typically requires prolonged annealing at higher temperatures (e.g., 1 h at 200 °C), HC-ZnO achieves the necessary crystallinity after just 10 min at 80 °C [6,7,10]. This lower thermal budget and simpler processing route further facilitate the translation of our dual-doping strategy into scalable, energy-efficient manufacturing conditions. The reduction of crystal defects in the modified ZnO films was further confirmed through photoluminescence (PL) spectroscopy. A broad green emission band with a maximum at around 550 nm is characteristic for ZnO NCs which originates from crystal defects such as oxygen vacancies [39]. Electrons or holes can get trapped at these defect sites, influencing the conductivity, optical properties, and charge carrier recombination dynamics of ZnO [39]. A substantial reduction in the PL signal intensity was consistently detected in all samples treated with Mg [24] and Cs [25], aligning well with previous works (see Fig. 4c). This observation strongly supports the hypothesis of reduced defect sites achieved through effective defect passivation via metal ion treatment. Therefore, the reduction of crystal defects directly contributes to an improved charge transport and consequently optimizes the performance parameters of the device, especially Jsc and FF, as demonstrated in our CsMg-ZnO champion cell. These findings align well with previous studies on doped ZnO, where diverse dopants have shown distinct advantages. For instance, NaCl passivation reduces trap density and boosts PCE, K<sup>\*</sup> doping shifts the Fermi level to strengthen the internal electric field, and In<sup>3+</sup> doping improves charge transport dynamics [20–22]. Similarly,  $Mg^{2+}$  enhances  $J_{sc}$  by improving crystallinity and reducing defects, while Cs\* improves surface roughness and increases FF [23,24, 26,27]. By combining Mg<sup>2+</sup> and Cs<sup>+</sup> in our films, we integrate multiple beneficial effects-defect passivation, improved crystallinity, and optimized interfaces-resulting in the marked enhancements in FF and J<sub>sc</sub> observed here. UV-Vis spectroscopy was used to investigate the effect of ZnO defect passivation on the transparency of the ZnO layers (see Fig. 4d). Interestingly, it shows an enhanced transmission for all modified samples. Higher transmission facilitates the efficient collection of high-energy photons within the UV-range by the absorber layer, as demonstrated in fig. S7 [23,24]. Thus, the increased photon collection represents an additional parameter contributing to increased charge transport,  $J_{sc}$ , and overall device performance. The surface topography of ZnO films was examined using atomic force microscopy (AFM) as illustrated in Fig. 5. The analysis reveals that the metal ion treatment contributes to the improvement of ZnO film surface roughness, potentially enhancing the FF of solar cells and promoting efficient charge transport at the ETL-Absorber interface (see Fig. 5a-d). The corresponding root mean square (RMS) values for pristine ZnO, Mg-ZnO, CsMg-ZnO, and Cs-ZnO are 2.376, 2.234, 1.964, and 1.959 nm, respectively, as shown in Fig. 5f. The reduced surface roughness observed in metal ion treated ZnO films indicates a more uniform



**Fig. 5.**  $4 \times 4 \mu m^2$  3D AFM images of blade coated ZnO thin films: In the first row, comparing the modified ZnO films based on the ternary solvent system (a) Mg-ZnO, (b) CsMg-ZnO, and (c) Cs-ZnO. In the second row, comparing the pristine ZnO film of the binary and ternary solvent system: (d) pristine ZnO with the ternary solvent system, (e) pristine ZnO with the binary solvent system. The corresponding RMS values in nanometres are listed in (f).

nanocrystal arrangement and the effective passivation of defect-rich surface sites. Both Mg and Cs treatments have been shown to influence ZnO growth kinetics and surface chemistry, leading to fewer grain boundaries and smoother films. By occupying or neutralizing surface defect states, these metal ions minimize charge traps and improve the interfacial contact with the PbS absorber layer. Such morphological and chemical modifications are crucial for improving charge extraction and reducing interfacial recombination, thereby contributing to the enhanced FF and  $J_{sc}$  in our solar cells. This passivation effect may alter surface energies, reducing the occurrence of agglomerations during film deposition and resulting in a smoother film. Additionally, the enhanced colloidal stability of the treated ZnO nano-inks supports this finding.



Fig. 6. High resolution XPS profiles of pristine ZnO and CsMg-ZnO films: (a) Mg 2p spectra, (b) Cs 3d spectra, and the XPS spectra with fittings of the O 1s core level spectra for (c) pristine ZnO and (d) CsMg-ZnO.

Improved crystallinity, as shown in Fig. 4b, likely contributes to fewer grain boundaries, further promoting a more homogeneous and smoother film. Mg was identified as the most effective in enhancing crystallinity. However, its impact on the film formation and surface smoothness of the ZnO films was limited, resulting in only a moderate increase in FF (see Fig. 2c-Table 1). In contrast, Cs, demonstrated good film formation behaviour, with a nearly 20 % reduction in the surface roughness RMS value. This reduced surface roughness, consistent with findings in other studies [26, 27, 40] led to a more substantial enhancement in FF and J<sub>sc</sub> compared to Mg-treated films (see Table 1). By incorporating both Cs and Mg ions into a single ZnO film, an optimal balance between crystallinity, defect reduction, transmission and surface morphology was achieved. Details on the effect of the ternary solvent system on the ZnO surface morphology are presented in Fig. 5d-e and will be discussed in depth in the solvent engineering section. To look at the chemical composition of the samples we conducted x-ray photoelectron spectroscopy (XPS) measurements and energy dispersive x-ray (EDX) analysis. Fig. 6a-b shows the high-resolution XPS peaks of Mg 2p and Cs 3d, which confirm the successful incorporation of Cs and Mg into the ZnO films. The Mg 2p peak emerges at 51.6 eV, while the Cs 3d peaks are observed at 726.2 eV and 740.3 eV, aligning well with previous studies [25,41,42]. In addition, the corresponding EDX spectra of the CsMg-ZnO films are shown in Fig. S8, which approve the incorporation of both metal ions into the ZnO film. The Zn 2p core line spectrum reveals two distinct peaks at 1022.1 eV and 1045.1 eV for Zn 2p 3/2 and Zn 2p 1/2, respectively (see Fig. S9a - the corresponding XPS survey spectra can be found in Fig. S9b) [43]. The observed Zn 2p peaks undergo a marginal shift of around 0.5 eV towards higher binding energy in CsMg-modified ZnO, which is in good agreement with other findings. [24, 44] Furthermore, as depicted in Fig. 6c-d, the core-level spectrum of oxygen O 1s is presented for ZnO and CsMg-ZnO films. The binding energy centred at 531.4 eV for pristine ZnO and 531.5 eV for CsMg-ZnO corresponds to lattice oxygen. The peak at a higher energy of 533.1 eV for pristine ZnO and 533.3 eV for CsMg-ZnO is attributed to surface oxygen, specifically electrostatically bound hydroxyl (OH) groups.[22, 45] Through surface integral calculations, the ratio between the lattice oxygen peak and the surface oxygen peak was determined to be 0.84 (Fig. 6c and 45.7 %: 54.3 %) for pristine ZnO, which is distinctly shifted to approximately 1.10 (Fig. 6d and 51.7 %: 48.3 %) for CsMg-ZnO. The attenuated O 1s peak at 533.3 eV in CsMg-ZnO, along with the reduced PL intensity, provides direct evidence for defect passivation by Mg and Cs. Previous studies have shown that introducing such metal ions can decrease oxygen vacancy density and improve the overall electronic structure of ZnO films [24,25]. This defect passivation decreases trap-assisted recombination, enhances electron transport, and better aligns the energy levels for charge extraction. In turn, these electronic improvements are manifested in the pronounced gains in device performance, including higher J<sub>sc</sub> and FF. This phenomenon has been documented in several prior studies involving various metal ion treatments (e.g., Na<sup>+</sup>, K<sup>+</sup>, In<sup>3+</sup>,  $Mg^{2+}$ ,  $Cs^+$ ) [20–25]. Notably, defect passivation is also apparent in our dual metal ion treatment approach contributing to improved charge transport, conductivity and  $J_{sc}$  within the solar cells. Additionally, UPS measurements were carried out to further understand the performance improvement by the dual metal ion treatment via establishing an electronic structure diagram. The determined secondary electron cut-off, combined with the measured valence band maximum (VBM) (see Figs. S10a-b) and the optical band gap deduced by a Tauc plot (see Fig. S10c), lead to the electronic structure diagram depicted in Fig. S10d (the absorption data used for the Tauc plot diagram are shown in Fig. S11). It illustrates that the introduction of Cs and Mg yields a VBM positioned a bit further away from the Fermi level  $(-3.15 \text{ eV vs } E_F)$  than the pristine ZnO (-3.06 eV vs E<sub>F</sub>). This shift implies an enhanced hole-blocking character at the interface with the PbS absorber layer, preventing flow back. The conduction band offset between the absorber and the ETL is also increased with the introduction of Cs and Mg (from +0.39 eV to +0.32 eV), favouring electron transfer. These phenomena

contribute to the increase in conductivity and  $J_{SC}$ . Due to the superior performance of CsMg-ZnO solar cells, we describe step by step the optimization process of the ZnO nano ink designed for doctor blading in the following section.

Fig. 5:  $4 \times 4 \mu m^2$  3D AFM images of blade coated ZnO thin films: In the first row, comparing the modified ZnO films based on the ternary solvent system (a) Mg-ZnO, (b) CsMg-ZnO, and (c) Cs-ZnO. In the second row, comparing the pristine ZnO film of the binary and ternary solvent system: (d) pristine ZnO with the ternary solvent system, (e) pristine ZnO with the binary solvent system. The corresponding RMS values in nanometres are listed in (f).

Solvent engineering made an important contribution to the successful development of a printable ZnO nano ink. Today the standard solvent for spin-coated ZnO-ETLs in PbS-CQDSCs is a mixture of MeOH and CHCl<sub>3</sub>. Both solvents have relatively low boiling points (T<sub>boil(MeOH)</sub> = 65 °C,  $T_{boil(CHCl3)}$  = 61 °C) and very high vapor pressure ( $p_{vap(MeOH)}$  = 169 hPa at 25 °C,  $p_{vap(CHCl3)} = 210$  hPa at 20 °C), which leads to rapid film drying and is therefore suboptimal for doctor blade coating [30,31]. One strategy to optimize the uniformity of the coating is to adjust the solvent components of the ink [46]. In printing, the flow of ink is crucial to the formation of droplets and thin films and the quality of the final printed image. Two main types of flow are present in printing: the Marangoni flow and the capillary flow [47]. (i) Capillary flow, driven by nonuniform evaporation-induced surface distortion, leads to outward convective flows and excessive mass transport to the film's edge. This is a common undesirable effect known as the coffee-ring effect, often observed in printed films. (ii) Marangoni flow is driven by surface tension gradients caused by concentration differences during evaporation and solidification. It moves from regions of higher particle concentration (associated with high evaporation rates) to areas of lower particle concentration (associated with low evaporation rates) along the solution-air interface. Importantly, Marangoni flow counteracts the outward particle transport induced by capillary flow, playing a key role in achieving thin film uniformity by balancing excessive mass transport. Since the interaction of these two flow types can have a substantial impact on the quality of the final printed image, a solvent engineering strategy was introduced to further improve the printing properties of the nano ink. Thereby, a ternary solvent system consisting of a combination of CHCl<sub>3</sub>: MeOH:2-ME in a 1:1:1 ratio (vol.-%) with a concentration of 100 mg/mL (see Fig. S12) and a 1:1 mixing ratio of Cs-ZnO and Mg-ZnO proved to be effective. The physical properties of 2-ME give the ternary system special printing characteristics adapted to the meniscus-controlled blade coating process, leading to an optimized balance between capillary flow and Marangoni flow. The increased viscosity ( $\eta_{2-ME} = 1.7$ ) and polarity  $(p_{2-ME} = 5.5)$  of the ternary system improves ink wettability while the high boiling point ( $T_{boil(2-ME)} = 125$  °C) and low vapor pressure ( $p_{vap}$ (2-ME) = 10 hPa at 20 °C) of 2-ME results in modified film drying behaviour. The findings demonstrate an optimal ink distribution across the ITO surface, leading to a uniform film formation, as verified by the AFM analysis. Fig. 5d-e provides a direct comparison of ZnO films produced through the binary and the ternary solvent systems. It reveals a noteworthy enhancement in surface smoothness, as evidenced by the RMS values of 4.819 nm for the binary system and 2.376 nm for the ternary solvent system (additional AFM images and photographs of ZnO films are displayed in Fig. S13, demonstrating an inhomogeneous film formation when using the conventional binary solvent system). This substantial optimization in film homogeneity contributes to the enhancement of both solar cell efficiency and device reproducibility as illustrated in Fig. 7 and Table 2.

# 4. Conclusion

In this work, we successfully developed a printable ZnO-ETL nanoink using a low-temperature dual metal ion treatment and solvent engineering strategy. The incorporation of Mg and Cs ions into the formulation allowed us to fine-tune crystallinity, defect density, surface



Fig. 7. Performance comparison of CsMg-ZnO based solar cell devices made of the ternary solvent system nano ink (blue: CHCl<sub>3</sub>:MeOH:2-ME) and the binary solvent system nano ink (orange: CHCl<sub>3</sub>:MeOH) including (a) PCE (b) FF (c) J<sub>sc</sub> and (d) V<sub>oc</sub> box plot diagrams. (device architecture: Glass/ITO/CsMg-ZnO/PbS-PbI<sub>2</sub>/PbS-EDT/Au).

 Table 2

 Illustration of the corresponding average value for the ternary and binary solvent systems.

ETL	PCE <sub>mean</sub> [%]	FF <sub>mean</sub> [%]	Jsc <sub>mean</sub> [mA/ cm <sup>2</sup> ]	Voc <sub>mean</sub> [V]
Ternary CsMg- ZnO	$8.40\pm0.85$	$\textbf{57.8} \pm \textbf{5.32}$	$23.25 \pm 1.62$	$0.61\pm0.01$
Binary CsMg- ZnO	$2.41 \pm 2.03$	$\textbf{33.4} \pm \textbf{13.66}$	$12.21\pm5.68$	$0.54\pm0.15$

passivation, surface morphology, and bandgap alignment, leading to improved electrical conductivity. By optimizing the solvent mixture (CHCl<sub>3</sub>:MeOH:2-ME in a 1:1:1 ratio), we achieved a champion PbS-CQDSC device with a FF of 63 % and a  $J_{sc}$  of 24.74 mA/cm<sup>2</sup>, resulting in a PCE of 9.53 %. This represents a 59 % increase in efficiency compared to the control device. More importantly, our printing approach demonstrates scalability and manufacturing potential (see SI, Tables S2 and S3), as shown by the enhanced reproducibility. The improved average PCE of 8.4 %  $\pm$  0.85 for CsMg-ZnO devices exceeds the control device's average PCE of 2.8 %  $\pm$  2.35. While efficiencies beyond 15 % have been demonstrated using spin coating and vapor deposition methods at the lab scale [3,5–8], scaling these approaches to industrial-level throughput remains challenging. Achieving nearly 10 % efficiency via doctor-blade-coated ETLs and absorber layers bridges the

gap between lab-scale record efficiencies and commercially viable manufacturing techniques, representing a critical step toward the large-scale deployment of PbS CQD photovoltaics.

#### CRediT authorship contribution statement

Rico Holfeuer: Writing – review & editing, Writing – original draft, Validation, Investigation, Conceptualization. Clément Maheu: Writing – review & editing, Investigation. Hannah Illner: Writing – review & editing, Investigation. Rik Hoojier: Writing – review & editing, Investigation. Harishankar Balakrishnan: Writing – review & editing, Investigation. Benjamin März: Writing – review & editing, Investigation. Soroush Lotfi: Writing – review & editing, Investigation. Soroush Lotfi: Writing – review & editing, Investigation. Knut Müller-Caspary: Writing – review & editing, Investigation. Knut Müller-Caspary: Writing – review & editing, Investigation. Thomas Bein: Writing – review & editing, Resources. Jan P. Hofmann: Writing – review & editing, Investigation. Tayebeh Ameri: Writing – review & editing, Supervision, Conceptualization. Achim Hartschuh: Writing – review & editing, Supervision, Conceptualization. AmirAbbas YousefiAmin: Writing – review & editing, Supervision, Resources, Project administration, Conceptualization.

#### Declaration of competing interest

The authors declare that they have no known competing financial

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interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtener.2025.101813.

# Data availability

The authors are unable or have chosen not to specify which data has been used.

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