



Enhanced efficiency of Sb_2S_3 solar cells via heterojunction interfacial $\text{MgCl}_2\text{-CdCl}_2$ mixed treatment

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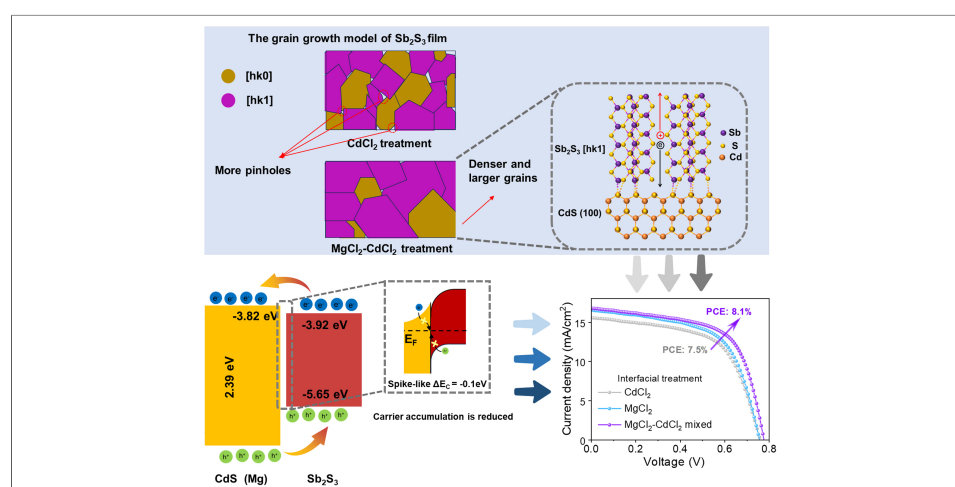
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Abstract

Antimony sulfide (Sb_2S_3) solar cells exhibit significant potential in tandem and indoor photovoltaic applications. The quality of cadmium sulfide (CdS)/ Sb_2S_3 heterojunction, affected by energy-level misalignments and lattice-mismatch defects, is crucial for achieving high-performance devices. Herein, we propose a $\text{MgCl}_2\text{-CdCl}_2$ mixed treatment strategy for the $\text{CdS}/\text{Sb}_2\text{S}_3$ interface to suppress interfacial recombination caused by defects and energy band offsets. The obtained preferentially [100]-oriented CdS film effectively mitigates lattice mismatch and induces the subsequent hydrothermal deposition of a well-crystallized, vertically oriented Sb_2S_3 absorber. The $\text{MgCl}_2\text{-CdCl}_2$ mixed treatment introduces Mg^{2+} doping in the CdS layer, achieving an enhanced surface potential and well-matched interfacial energy band alignments. The $\text{CdS}/\text{Sb}_2\text{S}_3$ heterojunction interface forms a spike-type energy band structure with a small conduction band offset. Compared with the conventional CdCl_2 treatment, the $\text{MgCl}_2\text{-CdCl}_2$ mixed-treated device exhibits a stronger built-in electric field (1.31 V) and low-temperature activation energy (1.63 eV),

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indicating the suppression of carrier recombination. Consequently, the champion Sb_2S_3 solar cells achieve an improved efficiency from 7.5% to 8.1%. This heterojunction treatment strategy is expected to provide an effective method for fabricating high-performance inorganic thin film solar cells.

INTRODUCTION

Antimony sulfide (Sb_2S_3) solar cells have received widespread attention owing to their non-toxicity, low cost, and high stability. Sb_2S_3 films possess a relatively low melting point ($\sim 550^\circ\text{C}$), enabling the production of highly crystalline films at relatively low temperatures and thereby reducing energy consumption during device fabrication^[1]. Additionally, their bandgap (1.7 eV) is suitable for applications in Si-based top cells^[2], indoor photovoltaics^[3,4], photodetectors^[5,6], and optical communication systems^[7]. According to the Shockley-Queisser limit theory^[8], the theoretical maximum power conversion efficiency (PCE) for a single-junction Sb_2S_3 solar cell can reach 28%. After over a decade of development, the highest PCE of Sb_2S_3 solar cells was reported to be 8.26%^[9]. Despite this progress, the performances of Sb_2S_3 solar cells remain substantially lower than those of established technologies. The main issue is the large open-circuit voltage (V_{oc}) loss caused by interfacial defects and recombination. The performance of the Sb_2S_3 solar cell can be significantly improved after addressing the limiting factors of the heterojunction interface.

Cadmium sulfide (CdS) with good photovoltaic properties is widely used as an electron transport layer (ETL) in Sb_2S_3 solar cells. However, the interfacial energy-level misalignment and lattice mismatch at the CdS/ Sb_2S_3 heterojunction lead to severe interface recombination and carrier loss^[10,11]. In addition, the high absorption of the CdS layer in the short-wavelength region (300–500 nm) reduces the light utilization efficiency of the Sb_2S_3 absorber layer^[12]. Therefore, the CdS/ Sb_2S_3 heterojunction quality is particularly important for the performance of the device. Currently, there are numerous heterojunction optimization strategies, such as ion doping, interface modification, energy level regulation, and post-processing^[13–16]. Shen *et al.*^[17] inserted an ultra-thin amorphous ETL at the heterojunction, which can improve interfacial carrier extraction. Liu *et al.*^[18] developed a core/shell-structure interfacial layer in the Sb_2S_3 solar cell, boosting the photovoltaic performance. According to reports, cations (e.g., Al^{3+}) can be doped into CdS to replace Cd^{2+} , forming substitution defects^[19] and increasing the N-type doping concentration. In addition, the monovalent cation Ag^+ was doped in CdS, which enhances the conductivity of the CdS film anomalously and reduces its parasitic absorption simultaneously^[20]. Interface post-processing is an effective approach to achieve interface optimization and suppress interfacial recombination effects. Most reported studies on halide-based treatments have focused on the absorber layer surface of Sb-based solar cells. Zhao *et al.* regulated an alkali metal fluoride post-treatment to fabricate high-performance $\text{Sb}_2(\text{S},\text{Se})_3$ solar cells by improving absorber crystallinity and conductivity^[21]. Shen *et al.* developed a PbCl_2 post-treatment onto the Sb_2S_3 back surface to passivate interfacial defects and reduce non-radiative recombination of the Sb_2S_3 solar cell, resulting in a significant increase in fill factor (FF)^[22]. This indicates that halide-based strategies to treat the absorber layer help to enhance crystallization and improve orientation. For CdS treatment, SbCl_3 treatment has been shown to improve the quality of CdS films and optimize energy band alignment at the CdS/ Sb_2S_3 interface^[23]. At present, the CdCl_2 treatment for CdS films is a widely used processing method. It can broaden the bandgap of CdS and reduce S vacancy defects in CdS^[24]. Besides, the Cl doping of the absorber layer can passivate S vacancy defects^[25], contributing to the suppression of V_{oc} loss.

In this work, we propose a MgCl_2 - CdCl_2 mixed heterojunction interface treatment strategy for Sb_2S_3 thin-film solar cells to suppress interfacial recombination and improve device efficiency. The introduction of Mg^{2+} into CdS film induces preferential growth of cubic-phase CdS along the (100) crystallographic plane, promoting vertical orientation growth in the absorber. Meanwhile, this mixed treatment optimizes the band alignment

at the CdS/Sb₂S₃ heterojunction interface, effectively suppressing carrier accumulation at the interface. Systematic characterizations such as Kelvin probe force microscopy (KPFM) and variable-temperature measurement are used to demonstrate the physical mechanism of the photocarrier transport and recombination. The results show that the treatment enhances the built-in electric field and low-temperature activation energy (E_a), thereby overcoming V_{oc} loss. The good crystallinity, interface defect passivation, and well-matched energy band alignments enable 8.1% efficiency of the Sb₂S₃ solar cells.

EXPERIMENTAL

Preparation of CdS film and treatment

CdS films were prepared on fluorine-doped tin oxide (FTO) substrates using the chemical bath method (CBD). First, FTO glass substrates were ultrasonically cleaned for 20 min each in detergent, anhydrous ethanol, acetone, and deionized water, followed by nitrogen drying. Next, 32 mL of 15 mM CdSO₄ (99.99%, Macklin) and 40 mL of aqueous ammonia solution (25%-28%, Sinopharm) were sequentially added to 220 mL of deionized water, preheated at 66 °C for 2 min, and then 16 mL of 1.5 M thiourea (99.0%, Sinopharm) was added to the solution. The FTO substrate was vertically immersed in the precursor solution and maintained at 66 °C for 18 min to obtain a CdS layer approximately 60 nm thick. The MgCl₂-CdCl₂ mixed heterojunction interface treatment of CdS films was utilized by spin coating the MgCl₂-CdCl₂ mixed methanol solution at 4,000 revolutions per minute (rpm) for 20 s. Under fixing CdCl₂ concentration of 15 mg/mL, the Mg/Cd molar ratios are controlled as 0.45, 0.9, and 1.35 by regulating MgCl₂ concentration of 5, 10, and 15 mg/mL. The CdS samples were dried in air at 80 °C for 5 min to remove residual solvent and then annealed at 400 °C for 10 min.

Device fabrication

Sb₂S₃ films were prepared via a hydrothermal deposition method using C₈H₄K₂O₁₂Sb₂·3H₂O (99.9%, Aladdin, Shanghai, China) and Na₂S₂O₃·5H₂O (99.99%, Aladdin) as the source materials for antimony and sulfur, respectively. Specifically, 40 mL of 40 mM C₈H₄K₂O₁₂Sb₂·3H₂O solution was stirred for 3 min until the solution color changed from transparent to slightly yellow. The mixed solution was transferred to a 50 mL polytetrafluoroethylene (Teflon) reaction vessel, which was then sealed within a stainless-steel reaction vessel. The mixture was maintained at 130 °C for 180 min to obtain the Sb₂S₃ precursor film. The deposited film is then annealed in a rapid thermal annealing tube furnace (OTF-1200X, Kejing, Hefei, China) under an Ar atmosphere at 370 °C for 5 min. The Spiro-OMeTAD (2,2',7,7'-tetrakis-(N,N-di-4-methoxyphenyl amino)-9,9'-spirobifluorene) hole transport layer was prepared by spin-coating, with the method consistent with previous reports, at a spin speed of 4,000 rpm for 20 s, followed by annealing at 105 °C for 10 min on a hot plate. Finally, gold electrodes (device area of 0.09 cm²) were prepared using thermal evaporation, forming the solar cells in the configuration of FTO/CdS(treated)/Sb₂S₃/Spiro-OMeTAD/Au.

Characterizations and measurements

The surface and cross-sectional morphologies and the elemental ratio of the Sb₂S₃ film were examined using a double-beam field emission scanning electron microscope (SEM, Helios G4 CX, Thermo Fisher Scientific, Hillsboro, OR, USA). The X-ray diffraction (XRD) was measured by Rigaku SmartLab (Cu K α radiation, 40 kV, 30 mA; scan range 10°-70°, scan rate 10°/min; Rigaku, Tokyo, Japan). X-ray photoelectron spectroscopy (XPS) was carried out using a RESOLVE 120MCD5 system (Thermo Fisher Scientific), and ultraviolet photoelectron spectroscopy (UPS) was performed with a Thermo Fisher ESCALAB 250Xi spectrometer (Thermo Fisher Scientific) under a bias of -5 V. The surface potential and surface conductivity distributions of the CdS and Sb₂S₃ films were measured by KPFM (Bruker Dimension Icon, Billerica, MA, USA). Current density-voltage (J - V) curves of the devices under 100 mW/cm² illumination and a limited area of 0.09 cm² were measured using a solar simulator (SUN 2000, ABET Technologies, Milford, CT, USA) and a power meter (Keithley 2400 SourceMeter, Keithley Instruments, Cleveland, OH, USA). External

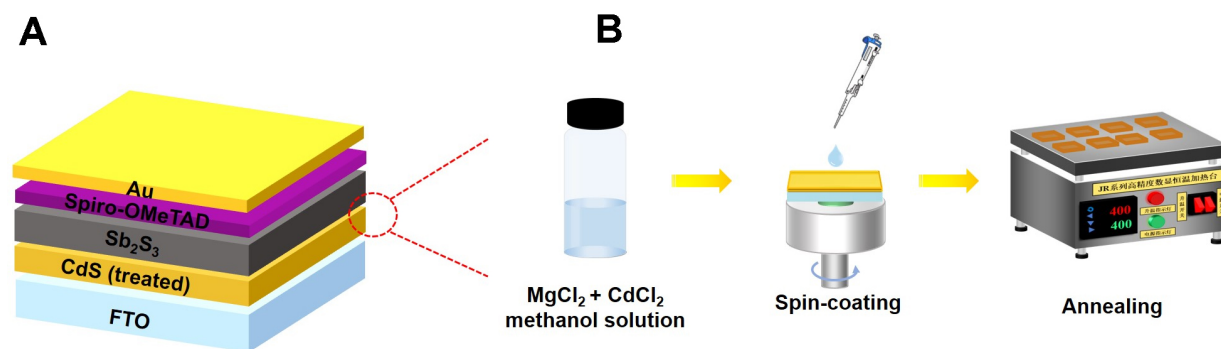


Figure 1. (A) Schematic diagram of the Sb_2S_3 device structure, (B) Interface processing diagram. CdS: Cadmium sulfide; FTO: fluorine-doped tin oxide.

quantum efficiency (EQE) spectra were recorded with a QE system (SCS100, Zolix Instruments, Beijing, China; CROWNTECH, Beijing, China) over the 300–800 nm range. Dark-state current-voltage curves were obtained using a semiconductor tester (FS-Pro, PRIMARIUS, Shanghai, China). Electrochemical impedance spectroscopy (EIS) measurements were carried out on an electrochemical workstation (SP-200, Bio-Logic Science Instruments, France) at a bias potential of 0.50 V in the dark with a frequency range of 1 Hz to 1 MHz. Capacitance-voltage (C-V) characteristics were measured using a semiconductor parameter analyzer (Keithley 4200-SCS, Keithley Instruments) at 50 kHz frequency and a direct-current (DC) bias from -0.8 V to 0.8 V.

RESULTS AND DISCUSSION

Figure 1A depicts the typical planar structure of the fabricated Sb_2S_3 device in the configuration of FTO/CdS/ Sb_2S_3 /Spiro-OMeTAD/Au. The Sb_2S_3 thin film is deposited on the FTO/CdS substrate by the hydrothermal method. The quality of the CdS/ Sb_2S_3 heterojunction interface plays a critical role in achieving efficient carrier separation and transport. To address issues of heterojunction interfacial recombination, the CdCl_2 and MgCl_2 mixed treatment approach on CdS film is designed and illustrated in Figure 1B. The CdCl_2 and MgCl_2 powders are dissolved in anhydrous methanol to prepare a clear mixed solution. It is spin-coated onto the surface of the CdS layer, followed by an annealing treatment. We investigate the effects on device performances of three MgCl_2 concentrations (5, 10, and 15 mg/mL) under the fixed CdCl_2 concentration of 15 mg/mL. The obtained Mg/Cd molar ratios are 0.45, 0.9, and 1.35, respectively. As shown in Supplementary Figure 1, when the MgCl_2 concentration is 10 mg/mL (the Mg/Cd ratio of 0.9), the device achieves the best performance with significantly improved FF. The increased MgCl_2 concentration to 15 mg/mL deteriorates the efficiency. Furthermore, the optimal annealing temperature is determined to be 400 °C [Supplementary Figure 2] according to the PCE evolutions.

Currently, the CdCl_2 treatment for CdS ETL is a widely applied method in Sb_2S_3 solar cells. Based on this, we designed four sets of experiments to investigate the treatment effects, including untreated, only CdCl_2 -treated, only MgCl_2 -treated, and MgCl_2 - CdCl_2 mixed-treated CdS films. The surface morphologies of the CdS films under the different treatments are characterized by an SEM and shown in Figure 2A–D. Compared to the traditional CdCl_2 -treated film, the MgCl_2 - CdCl_2 mixed-treated (named MgCl_2 -M-treated) CdS film exhibits a flatter and denser surface morphology, which facilitates the uniform deposition of the Sb_2S_3 absorber layer for a dense heterojunction interface. Subsequently, the Sb_2S_3 thin films are deposited on the above CdS films, as shown in Figure 2E–H. The without (w/o) treated Sb_2S_3 film exhibits significantly smaller grain sizes, along with a high density of surface pinholes and particle accumulations that serve as effective trap centers, as demonstrated in Figure 2E. Although CdCl_2 -treated Sb_2S_3 films exhibit fewer surface particulates and larger grain sizes [Figure 2F], residual pinholes facilitate unintended contact between the

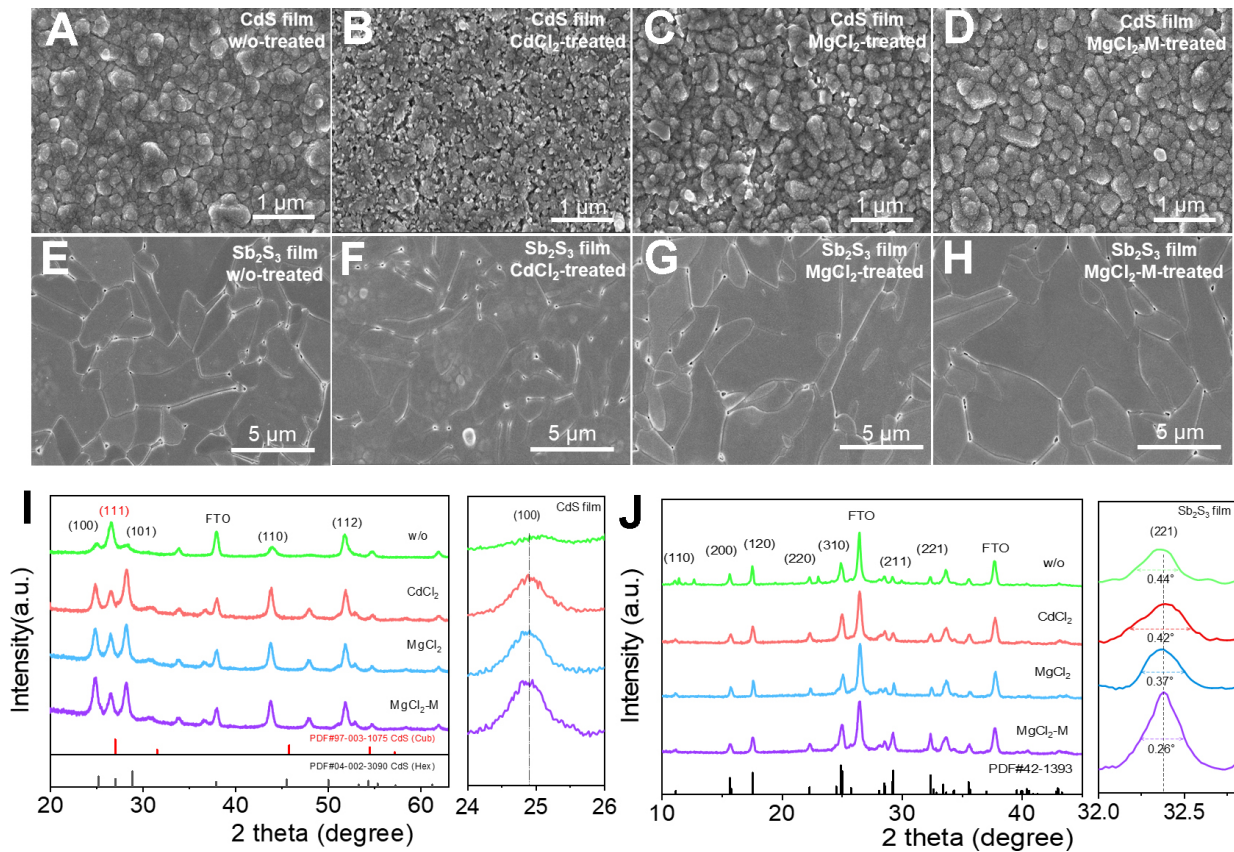


Figure 2. (A–D) SEM images of the CdS films, (E–H) SEM images of the Sb₂S₃ films, (I) GIXRD diffraction patterns of the CdS films, (J) XRD diffraction patterns of the Sb₂S₃ films. CdS: Cadmium sulfide; SEM: scanning electron microscope; GIXRD: grazing-incidence X-ray diffraction; XRD: X-ray diffraction.

hole transport layer and the Sb₂S₃ film. The Mg²⁺ introduction makes the CdS film much denser and promotes the crystallization of the absorber layer [Figure 2G]. In contrast, the Sb₂S₃ film deposited after MgCl₂-M treatment exhibits significantly larger grain sizes, higher film density, and reduced pinhole counts [Figure 2H]. Larger grain sizes typically imply fewer grain boundaries^[26], which helps reduce the probability of non-radiative recombination at grain boundaries and improves carrier transport properties within the absorber layer. Grazing-incidence X-ray diffraction (GIXRD) characterization is performed on the CdS film under the aforementioned conditions to investigate the influence of MgCl₂-M treatment on the crystal structure and orientation. As shown in Figure 2I, all the CdCl₂, MgCl₂, and MgCl₂-M treated CdS films display a mixed structure of cubic and hexagonal phases, with diffraction peaks corresponding to the (100), (111), and (101) crystal planes in ascending order of diffraction angle, while the untreated CdS film only shows a cubic structure. According to literature reports^[11,27], the (100) crystal plane of the CdS film is non-polar, which is favorable for Sb₂S₃ bonding on the CdS film, promoting the vertical growth of (Sb₄S₆)_n bands along the [hk1] direction (h, k = 0, 1, 2...), which is beneficial for carrier transport between bands. The XRD characterizations of the above Sb₂S₃ films are shown in Figure 2J. For ease of comparison, the peaks are normalized. It is clearly observed that the diffraction peak intensities of the (211) and (221) crystal planes are significantly enhanced. This indicates that MgCl₂-M treatment promotes the vertical growth of Sb₂S₃ film and enhances the carrier transport ability.

Sb₂S₃ thin-film solar cells in the configuration of FTO/CdS(treated)/Sb₂S₃/Spiro-OMeTAD/Au are constructed to evaluate the impact of MgCl₂-CdCl₂ mixed-treatment on performance. The statistical distributions of the V_{oc} , short-circuit current density (J_{sc}), FF, and PCE of the solar cells are presented in

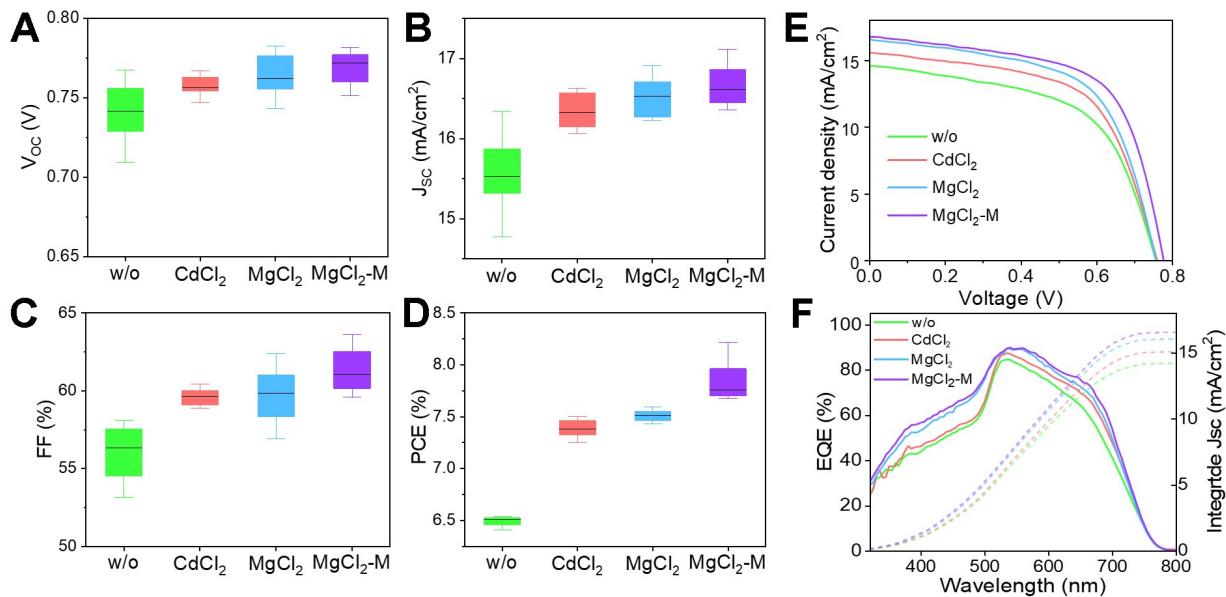


Figure 3. Photoelectric performance of the Sb_2S_3 solar cells. Statistical distribution of photovoltaic parameters for different treatment methods, including (A) V_{oc} , (B) J_{sc} , (C) FF, and (D) PCE; (E) J - V curves and (F) EQE spectra. V_{oc} : Open-circuit voltage; J_{sc} : short-circuit current density; FF: fill factor; PCE: power conversion efficiency; J - V : current density-voltage; EQE: external quantum efficiency.

Table 1. Photovoltaic parameters of the champion Sb_2S_3 devices

Devices	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
w/o	0.723	15.5	58.1	6.5
CdCl_2	0.757	16.5	60.3	7.5
MgCl_2	0.762	16.3	61.3	7.6
MgCl_2 -M	0.777	16.7	62.7	8.1

V_{oc} : Open-circuit voltage; J_{sc} : short-circuit current density; FF: fill factor; PCE: power conversion efficiency.

Figures 3A–D. The untreated device exhibits a V_{oc} of 0.723 V, a J_{sc} of 15.5 mA cm^{−2}, and a FF of 58.1%, resulting in a PCE of 6.51%. Compared to the untreated devices, the performance of devices using other processing methods has been significantly enhanced in V_{oc} and FF, with the most pronounced enhancement observed under MgCl_2 -M treatment conditions. **Figure 3E** displays the J - V curves of the w/o, CdCl_2 , MgCl_2 , and MgCl_2 -M treated devices under the standard air mass (AM) 1.5G light illumination. And the corresponding photovoltaic parameters are shown in **Table 1**. The MgCl_2 -M device exhibits a V_{oc} of 0.777 V with 7.6% enhancement, a J_{sc} of 16.7 mA cm^{−2}, and a FF of 62.7% with 7.9% increment, resulting in a PCE of 8.1%. Compared with the related halide post-treatments interface (such as SbCl_3 , PbCl_2 , NaF)^[21–23], the introduction of Mg^{2+} from MgCl_2 can control the bandgap of CdS film, energy band alignments, and interfacial defects, which exhibits competitive potential in increasement of V_{oc} and FF. Subsequently, we further characterize the EQE of these devices [**Figure 3F**]. The wavelength range for the EQE response of the Sb_2S_3 device is 300–780 nm. The MgCl_2 -M device demonstrates the highest photo response (up to 90%) in the range of 300–780 nm. MgCl_2 -M treatment effectively suppresses parasitic absorption in the CdS layer (within the 300–500 nm wavelength range), improving the utilization of incident sunlight. Additionally, the EQE spectrum in 600–780 nm has also improved slightly, which is attributed to the improved quality of the Sb_2S_3 film. According to the EQE spectra, the integrated current densities of the w/o, CdCl_2 , MgCl_2 , and MgCl_2 -M devices are calculated, which are consistent with the J_{sc} values obtained from the J - V curves.

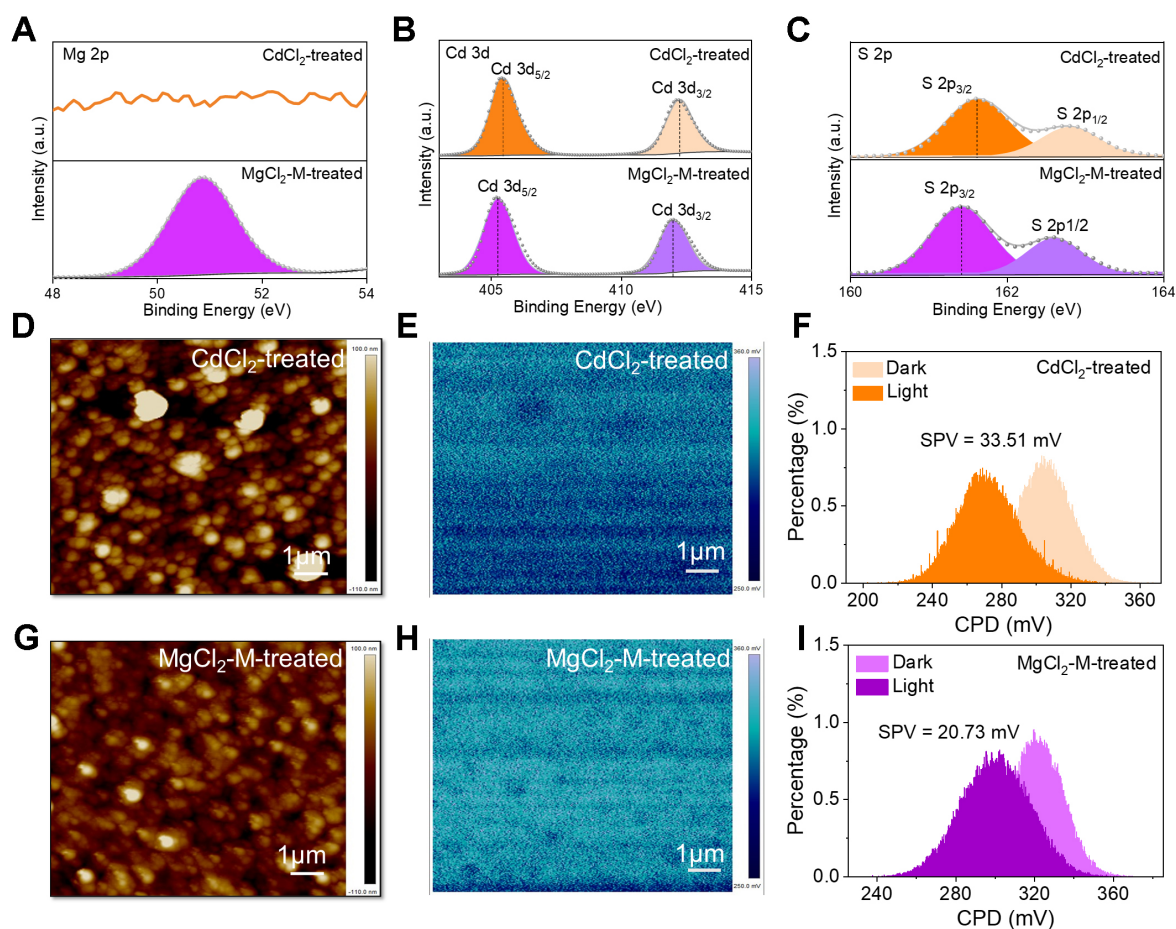


Figure 4. XPS spectra of (A) Mg 2p, (B) Cd 3d, and (C) S 2p. (D) and (G) AFM images; (E) and (H) KPFM images; (F) and (I) statistical potential distributions of CdCl₂ and MgCl₂-M treated CdS films. XPS: X-ray photoelectron spectroscopy; KPFM: Kelvin probe force microscopy; CdS: cadmium sulfide; SPV: surface photovoltage; AFM: atomic force microscope.

Considering the widespread use of CdCl₂ treatment, the following discussion focuses exclusively on a comparative study of CdCl₂ and MgCl₂-M treatments. The XPS is employed to analyze changes in elemental composition and chemical states in CdCl₂ and MgCl₂-M treated CdS layers [Figure 4A–C and Supplementary Figure 3]. The XPS spectra of all samples were calibrated using the C 1s peak at 284.8 eV as the binding energy reference. High-resolution spectra in the core-level regions, such as Cd 3d, S 2p, and Mg 2p, are deconvoluted to extract chemical state information of the relevant elements. The XPS spectrum of the MgCl₂-CdCl₂ mixed-treated sample [Figure 4A] clearly shows the characteristic Mg peak at 50.9 eV, which is absent in the control spectrum. This observation indicates successful Mg incorporation into the CdS buffer layer. Figure 4B presents the Cd 3d spectrum of the control CdS, with characteristic peaks at 405.2 eV (Cd 3d_{5/2}) and 412.3 eV (Cd 3d_{3/2}). Following MgCl₂-CdCl₂ mixed treatment, the Cd 3d peaks exhibit a shift toward lower binding energies. This shift indicates a reduction in the content of high-binding-energy components [CdO and Cd(OH)₂] on the surface of the treated sample, reflecting changes in the surface chemical environment^[20]. As shown in Figure 4C, after MgCl₂-CdCl₂ mixed treatment, the S 2p spectrum, featuring peaks at 161.6 eV (S 2p_{3/2}) and 162.9 eV (S 2p_{1/2}), presents a blue shift (lower binding energy), caused by the formation of S-Mg bonds on the CdS surface.

The surface morphology evolution and potential distribution are characterized by KPFM and shown in Figure 4D–F (CdCl₂-treated CdS sample) and Figure 4G–I (MgCl₂-M treated CdS sample). Compared to the surface roughness (43.7 nm) of the CdCl₂-treated CdS film (see Figure 4D), the mixed-treated CdS film

exhibits a reduced roughness of 22.6 nm (see Figure 4G). This improved surface smoothness facilitates more homogeneous deposition of the subsequent Sb_2S_3 absorber layer, thereby enabling the formation of a flatter and better-defined heterojunction interface. The MgCl_2 -M-treated CdS film exhibits higher and more uniformly distributed contact potential difference (CPD) values [Figure 4E and H]. This increase in V_{CPD} indicates a lower work function for the treated CdS, meaning its Fermi level (E_F) is closer to the vacuum level^[28]. Within the CdS/ Sb_2S_3 heterojunction architecture, this upward shift of the E_F in the CdS layer enhances quasi- E_F splitting, leading to an increased built-in potential (V_{bi}). This enhancement is a key factor contributing to the improvement in V_{OC} . The magnitude of surface photovoltage (SPV) is commonly associated with the surface defect density of semiconductor materials^[29]. To further evaluate the influence of MgCl_2 -M treatment on CdS film surface defect states, the CPD changes under dark and illuminated conditions are measured, as shown in Figure 4F and I. The CdCl_2 -treated CdS film exhibits an SPV of 33.51 mV, whereas the MgCl_2 -M-treated film exhibits a notably reduced SPV of 20.73 mV. The reduced SPV value suggests that MgCl_2 -M treatment effectively suppresses the surface defect density in the CdS film.

The band gap, band structure, and charge-transfer characteristics of the devices are used to determine interfacial energy-level alignments. As shown in the ultraviolet-visible absorption spectra (see Supplementary Figure 4A), the MgCl_2 -M-treated CdS film exhibits reduced absorption in the 300–500 nm region, thereby minimizing absorption losses. This enhanced optical transparency promotes greater photon transmission to the underlying Sb_2S_3 absorber layer. The fitted optical bandgaps of CdCl_2 -treated and MgCl_2 -M-treated CdS films are 2.39 and 2.38 eV, respectively [Supplementary Figure 4B and C]. The band gaps of the corresponding Sb_2S_3 films are the same 1.73 eV [Supplementary Figure 5], which is not affected by interface treatment. Furthermore, UPS is used to elucidate the regulatory mechanism of MgCl_2 -M treatment on the carrier dynamics of the Sb_2S_3 device. UPS can characterize the electronic structure of valence-band electrons and determine the EF and the valence-band position of a material by analyzing the cutoff edge and the Fermi edge^[30]. Figure 5A–D presents the UPS spectra of CdS and Sb_2S_3 films under distinct treatment conditions.

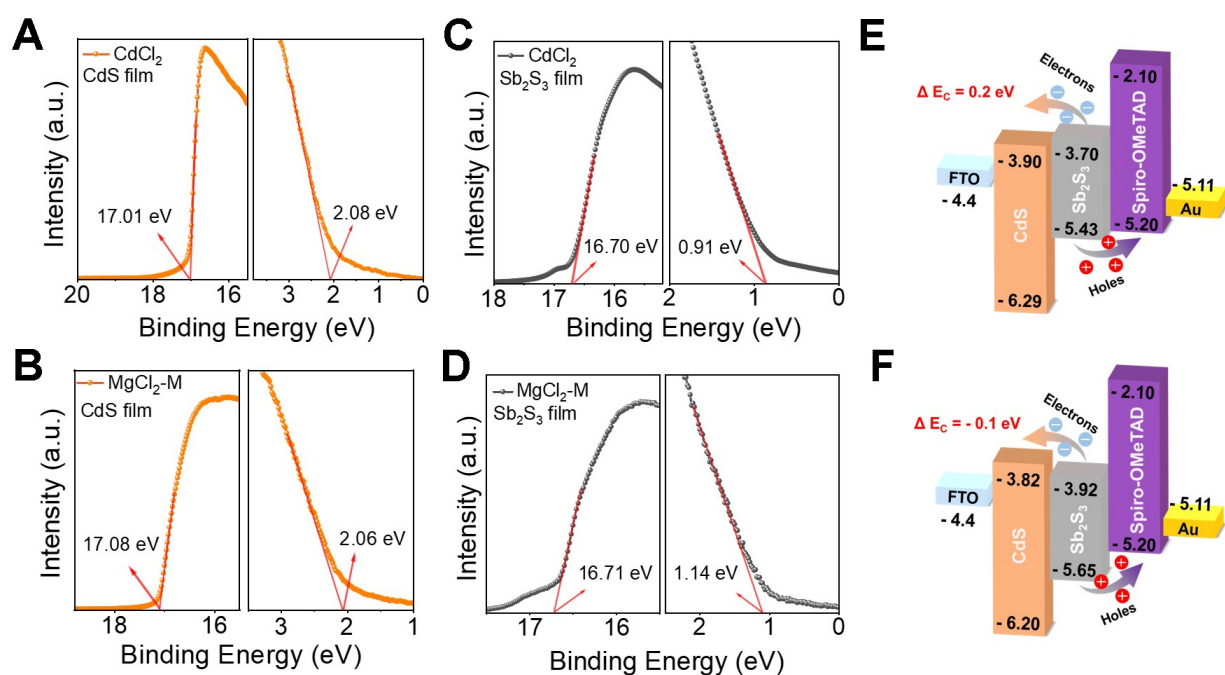


Figure 5. XPS spectra of (A) CdCl_2 -treated and (B) MgCl_2 -M-treated CdS films; XPS spectra of Sb_2S_3 films on (C) CdCl_2 -treated and (D) MgCl_2 -M-treated CdS films. Energy level diagrams of (E) the CdCl_2 and (F) MgCl_2 -M treated the device. XPS: X-ray photoelectron spectroscopy; CdS: cadmium sulfide; FTO: fluorine-doped tin oxide.

According to the cutoff edges (17.01 eV) and Fermi edges (2.08 eV) in Figure 5A, the calculated conduction band and valence band of the CdCl_2 -treated CdS film are -3.9 and -6.29 eV, respectively. The conduction band and valence band of the MgCl_2 -M-treated CdS film are -3.82 and -6.2 eV, respectively (see Figure 5B). The E_F of the CdS film shifts upward from -4.21 eV to -4.14 eV, reflecting an increased carrier concentration and enhanced electron collection. In addition, the calculated conduction bands of the two Sb_2S_3 films are -3.7 and -3.92 eV, and the valence bands are -5.43 and -5.65 eV, respectively [Figure 5C and D]. Based on these results, the band structure alignments at the CdS/ Sb_2S_3 interface after CdCl_2 and MgCl_2 -M treatment are shown in Figure 5E and F, respectively. The conduction band offset (CBO, ΔE_c) of the common CdCl_2 -treated CdS/ Sb_2S_3 interface is 0.2 eV, presenting a cliff-type alignment. Under this condition, electrons in the CdS conduction band readily transition to the valence band of Sb_2S_3 , resulting in recombination. The MgCl_2 -M treatment significantly modifies the energy level position of the conduction band. The CBO narrowed to -0.1 eV forms a spike-like energy band alignment, which reduces the back-contact barrier and enhances charge separation efficiency. Furthermore, it reduces the device's reverse saturation current and directly increases V_{OC} .

Carrier transport and collection characteristics are measured to probe the physical mechanism. The dark J - V measurements of the CdCl_2 and MgCl_2 -M treated devices are presented in Figure 6A. Both the Sb_2S_3 devices exhibit good rectifying behavior. Notably, the MgCl_2 -M-treated device displays a substantially lower reverse saturation current density (J_0) compared to the CdCl_2 -treated device [Supplementary Figure 6], indicating suppressed leakage pathways, due to reduced defect density and improved junction quality^[31]. The ideal factor (A) of the MgCl_2 -M-treated Sb_2S_3 device decreases significantly from 2.64 to 1.98. This parameter evolution indicates that MgCl_2 -M treatment effectively suppresses non-radiative recombination and leakage current paths, significantly improving the quality of the CdS/ Sb_2S_3 heterojunction interface, thereby reducing V_{OC} loss. The V_{bi} changes are quantified using the capacitance characteristic by the C^{-2} - V curve (see Figure 6B). The V_{bi} of the device after MgCl_2 -M treatment increases from 1.17 V to 1.31 V. The enhanced built-in electric field improves carrier separation and transport at the CdS/ Sb_2S_3 heterojunction interface, enabling

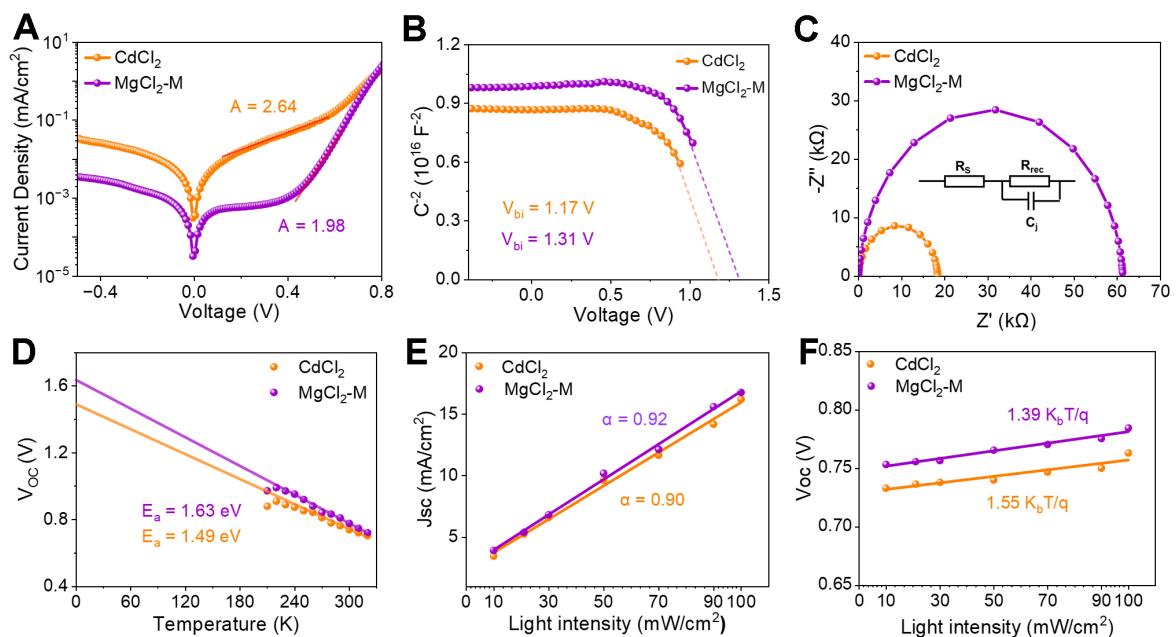


Figure 6. (A) Dark J - V characteristics; (B) $1/C^2$ - V plot; (C) Nyquist EIS curve of CdCl_2 and MgCl_2 -M treated films; (D) Temperature-dependent open-circuit voltage (V_{OC} - T) measurement; Light intensity dependent curves for (E) J_{SC} and (F) V_{OC} . V_{OC} : Open-circuit voltage; J_{SC} : short-circuit current density; J - V : current density-voltage; EIS: electrochemical impedance spectroscopy.

V_{OC} improvement. Furthermore, EIS also corroborates the above conclusions, with characterization conducted under dark conditions. Figure 6C shows the Nyquist plots for the two devices. Significantly, after $MgCl_2$ -M treatment, the recombination resistance (R_{rec}) increases from 8.3 k Ω to 28.6 k Ω . By applying a gradually increasing forward bias from 0 to 0.4 V, the trend of R_{rec} of the devices with the bias voltage is displayed in Supplementary Figure 7. The $MgCl_2$ -M treated device exhibits remarkably larger impedance magnitudes across and R_{rec} all the tested bias voltages compared to the control sample, manifesting weaker interfacial carrier recombination and better interface quality^[17]. These results indicate that the $MgCl_2$ -CdCl₂ mixed treatment effectively reduces the charge transfer barrier, promoting carrier separation and transport, thereby enhancing device performance.

Temperature-dependent J - V characterizations are used to calculate the E_a and analyze the defect recombination mechanism (see Supplementary Figure 8). By fitting the linear segment of the V_{OC} - T curve, the E_a at 0 K is obtained, as shown in Figure 6D. At 0 K, defects within the material are frozen, and electrons occupy the lowest energy levels^[32]. The V_{OC} limit is exactly equal to the bandgap. However, when interfacial defects are present, the E_a becomes smaller than the bandgap. The obtained E_a values of CdCl₂ and $MgCl_2$ -M treated devices are 1.49 and 1.63 eV, respectively. The larger E_a of $MgCl_2$ -M device indicates that interfacial defects of CdS/Sb₂S₃ are significantly passivated compared with the CdCl₂-treated device. Meanwhile, the E_a value of the mixed-treated device (1.63 eV) is in proximity to the bandgap of Sb₂S₃ (1.73 eV), suggesting an extremely low density of interface defects. To further understand the interface carrier recombination and transport characteristics of Sb₂S₃ devices, light intensity (I) dependent J_{sc} and V_{OC} relationships are analyzed and shown in Figure 6E and F, respectively. The J_{sc} - I curve follows the power-law principle $J_{sc} \propto I^\alpha$, where α is less than 1 due to the space charge effect. The α values for the CdCl₂-treated and $MgCl_2$ -M-treated devices are 0.90 and 0.92, respectively. A larger α indicates fewer carrier recombination in the $MgCl_2$ -M-treated device. Additionally, the relationship between V_{OC} and I can be expressed as $V_{OC} = nk_b T/q \ln(I)$ ^[33], where k_b is the Boltzmann constant, T is the temperature and q is elementary charge. Based on the slope of the fitted line, the n values for the control CdCl₂ and $MgCl_2$ -M treated devices are $1.55 k_b T/q$ and $1.39 k_b T/q$, respectively. In principle, this relationship indicates a defect-mediated Shockley-Read-Hall recombination mechanism^[34], with slope n values between 1 and 2, indicating that recombination occurs both at the interface and in the bulk material of the device^[15]. These results suggest that trap-assisted recombination processes are effectively suppressed in the $MgCl_2$ -M-treated devices, consistent with the observed improvements in PCE and FF.

CONCLUSIONS

In summary, we develop a $MgCl_2$ -CdCl₂ mixed interfacial treatment, enabling bidirectional optimization of the CdS/Sb₂S₃ heterojunction interface for efficient Sb₂S₃ thin film solar cells. This treatment effectively reduces parasitic absorption of the CdS film in the short-wavelength (300-500 nm) range, thereby enhancing the photon-harvesting efficiency of the absorber. Additionally, the improved surface quality of the CdS film enables the deposited Sb₂S₃ film to exhibit a significantly larger grain size, thereby reducing defects. Compared to the conventional CdCl₂-treated CdS film, the $MgCl_2$ -CdCl₂ mixed treatment introduces Mg²⁺ doping in the CdS layer, adjusting the interfacial energy band alignments. The enhanced surface potential and reduced SPV of the CdS film suppress surface defects. The CdS/Sb₂S₃ heterojunction interface achieves a transform from “cliff” to “spike” energy band structure and a small CBO (-0.1 eV), improving carrier separation efficiency. Based on these synergistic effects, the $MgCl_2$ -M device with a smaller J_0 and a large V_{bi} reveals a high-quality heterojunction. By temperature-dependent V_{OC} characterization, the optimal device E_a of 1.63 eV approaches the bandgap, resulting in effective suppression of nonradiative recombination. The champion Sb₂S₃ solar cell based on $MgCl_2$ -CdCl₂ mixed treatment achieves a PCE of 8.1%, with a V_{OC} of 0.777 V, a J_{sc} of 16.7 mA/cm², and an FF of 62.7%, respectively. This heterojunction interfacial treatment

strategy provides a promising approach to enhance the performance of Sb_2S_3 solar cells.

DECLARATIONS

Author contributions

Conceived the study and designed the experiments, device fabrication, and measurement methods: Deng, H.; Liu, Y.; Cheng, S.

Carried out the device fabrication and optimizations: Liu, Y.

Contributed to material characterizations, measurements, and data analysis: Liu, Y.; Peng, C.; Zhu, Q.; Wang, W.

Participated in manuscript discussions, revisions, and data interpretation: Cheng, S.; Wu, J.; Lai, Y.; Lin, P.

Primarily wrote and revised the manuscript: Liu, Y.; Deng, H.

All authors discussed the results and provided critical feedback on the manuscript.

Availability of data and materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Conflict of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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Supplementary Materials

[Supplementary Materials](#)

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