Effects of Incorporating PbS Quantum Dots in Perovskite Solar Cells Based on $\text{CH}_3\text{NH}_3\text{PbI}_3$

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Abstract: PbS quantum dots (QDs), prepared by the successive ionic layer adsorption and reaction (SILAR) method, are incorporated in perovskite solar cells based on $\text{CH}_3\text{NH}_3\text{PbI}_3$. Enhanced light absorption in the wavelength range of 330 - 1400 nm is observed, and the cell prepared with 2 SILAR coating cycles exhibits the best photovoltaic performance. It is observed that the PbS QDs can reduce the TiO_2 decomposition damage to the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films and promote the stability of the modified perovskite solar cells. Charge transfer dynamics in the perovskite solar cells is studied with intensity modulated photocurrent/photovoltage spectroscopy, and improved charge diffusion lengths are obtained for the modified cells, with the best value of 0.86 μm obtained for the device prepared with 2 SILAR coating cycles. This improvement could be attributed to the enhanced electron transport and reduced electron recombination processes in the device structures after incorporating PbS QDs.

Keywords: Perovskite solar cell, PbS quantum dots, IMPS/VS, Electron diffusion length

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1. Introduction

Achieving efficient and cost-competitive solar cells is still a challenge in the photovoltaic field, and a promising candidate that could fulfill these requirements is the organolead-halide-perovskite-based solar cells developed in recent years, which have rapidly grown to become the most efficient solution-processed photovoltaic and have reached a power conversion efficiency of 19.3% [1-4]. This high performance is attributed to the excellent electrical and optical properties of the organolead-halide-perovskite absorber $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃). It is well known that MAPbI₃ can absorb visible light in the wavelength range of 400 to 800 nm [5]. Expanding light harvesting in the near-infrared (NIR) region is one of the strategies that could further improve photovoltaic performance, and this approach has been widely utilized in quantum dot (QD) sensitized solar cells [6-8]. However, so far there are not many efforts on the exploration of this possibility in perovskite-based solar cells [9]. PbS nanocrystals, with a bulk band gap of 0.41 eV in the IR region, are considered as a particularly suitable semiconductor material for this purpose and could be size-tuned to be an efficient absorber in the NIR region [10-12]. In addition, due to the narrow band gap of PbS quantum dots, they could be utilized as a surface blocking layer between the nanocrystalline TiO₂ photoanode and the MAPbI₃ light absorber, which is similar to Sb₂S₃, and thus could reduce electron recombination between the two [13]. On the other hand, understanding charge transfer and recombination processes in solar cells is crucial for the design of efficient photovoltaic devices, and such processes in perovskite solar cells have been characterized by photoluminescence, time-resolved photoluminescence, and transient photocurrent/photovoltage decay measurements [14-16]. However, thus far there are only limited reports of utilizing the Intensity Modulated Photocurrent/Photovoltage Spectroscopy (IMPS/VS) technique to study perovskite solar cells [17], which is an important characterization method to inspect charge generation and transfer dynamics in sensitized solar

cells [18]. In this work we study the effects of incorporating PbS QDs in hybrid perovskite solar cells based on MAPbI₃. The structure of this hybrid TiO₂/PbS/MAPbI₃/P3HT/Pt solar cell is shown in Fig. 1a, in which the PbS QDs are utilized as NIR light absorber and surface blocking layer between the TiO₂ photoanode and MAPbI₃, MAPbI₃ is used as the visible light absorber, and P3HT is used as the hole transport material. Fig. 1b shows the energy level alignment in this hybrid solar cell structure when the TiO₂ photoanode film is fully covered by PbS QDs, in which the QD size is ~ 5 nm, corresponding to the size of the QDs prepared by 3 SILAR cycles in this study [19, 20]. From this energy level alignment it can be seen that the presence of a PbS layer between TiO₂ and MAPbI₃ is expected to facilitate electron transfer from MAPbI₃ to TiO₂. However, such a structure could also cause hole accumulation in PbS QDs and increase recombination possibility. The PbS QDs are deposited using the successive ionic layer adsorption and reaction (SILAR) method, and the effects of the SILAR coating cycle on light absorption and solar cell performance are studied. Utilizing the IMPS/VS technique, the charge transfer dynamics in the perovskite solar cells is characterized, and with the optimal PbS coating a long charge diffusion length of ~ 0.86 μ m is obtained.

2. Experimental methods

2.1 Sample preparation

Methylamine iodide (MAI) was synthesized by the dropwise addition of 5 mL hydroiodic acid (HI, aqueous, 57 wt %, Sigma-Aldrich) to a solution of 12 mL methylamine (CH₃NH₂, 33 wt % in pure ethanol, Aldrich) and 50 mL ethanol in an ice-water bath in a glove box filled with Argon. The cold solution was stirred for 4 h, and the solvent was allowed to evaporate overnight at room temperature. The crude CH₃NH₂I crystal was washed using diethyl ether (Sigma-Aldrich) three times and then dried at 70 °C in a vacuum oven for 24 h.

The obtained white solid crystal was used without further purification. The 40% MAPbI₃ precursor solution was prepared by dissolving equimolar amounts of 0.3625 g MAI and 0.1230 g PbI₂ (99.999%, ultra dry, Alfa Aesar) in anhydrous N, N-Dimethylmethanamide (DMF, anhydrous, Sigma-Aldrich) at 60 °C for 12 h.

A 0.5 μm-thick mesoporous TiO₂ film was deposited by spin-coating a TiO₂ paste (Dyesol 18NR-T, Australia, 20 nm) diluted in ethanol. The TiO₂ film was then sintered at 450 °C for 30 min.

The SILAR method was used to deposit PbS QDs on TiO₂ electrodes. The TiO₂ electrode was dipped into a 0.02 M Pb(NO₃)₂ (99.99%, Aldrich) in methanol solution for 1 min, and then was dipped into a 0.02 M Na₂S solution obtained by dissolving Na₂S·9H₂O (Sigma-Aldrich) in methanol/water mixed solvent for another 1 min. This SILAR process was repeated for 1 to 5 cycles to obtain PbS QD layers with different thicknesses. All of the procedures were carried out in a glove box filled with Ar.

40 wt % perovskite precursor solution was dropped on the PbS-covered TiO₂ electrode, and after resting for 1 min to let the material infiltrate into the mesoporous electrode film, the substrate with the precursor solution was rotated on a spin-coater at 2500 rpm for 30 s. The MAPbI₃ coated electrode was then placed on a hot plate at 100 °C for 15 min. A chlorobenzene (Alfa Aesar) solution containing 15 mg mL⁻¹ poly(3-hexylthiophene) (P3HT) (1-material), 287 mM 4-tert-butylpyridine (TBP, Aldrich), and 99.3 mM lithium bis-(trifluoromethylsulfonyl)imide salt (LiTFSI, Alfa Aesar) was used as the electrolyte, and was applied on the PbS/MAPbI₃/TiO₂ film under ambient conditions. When the electrolyte solution became viscous, a platinum plate was applied as the counter-electrode, and the sandwiched-structure was put into an oven at 80 °C for 15 min to completely dry the electrolyte solution and form a solid-state perovskite solar cell as shown in Fig. 1a.

2.2 Sample Characterization

Power X-ray diffraction (XRD) measurements were performed using a Rigaku Smartlab X-ray diffractometer (Tokyo, Japan) using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) with 2θ range from 10° to 80° for 5°min^{-1} step at ambient temperature. The size and morphology of the PbS/MAPbI₃ coated TiO₂ nanoparticles were analyzed by TEM using a JEOL 2010 microscope (Peabody, MA, USA). The morphology of the TiO₂/PbS/MAPbI₃ films with different SILAR cycles of PbS QDs was analyzed by a FEI Quanta FEG 450 field emission scanning electron microscope (FESEM, FEI, Hillsboro, OR, USA).

UV-Vis-NIR absorption spectra of TiO₂/PbS/MAPbI₃ films with different SILAR coating cycles were obtained by a Lambda 950 UV/VIS Spectrometer (PerkinElmer, Waltham, MA, USA). Cyclic voltammograms (CV) measurements of TiO₂/PbS/MAPbI₃ films were carried out using a Compact Stat.e10800 Electrochemical Analyzer (Ivium, Fernandina Beach, FL, USA) with a three-electrode configuration, in which the TiO₂/PbS/MAPbI₃ films served as the working electrode and were immersed in a 0.1 M LiClO₄/2-propanol (Fisher Scientific) solution. A Pt plate was used as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. The CV curves were obtained from -1.5 and 2.3 V (vs. the Ag/AgCl reference electrode) at a scanning rate of 0.05 V s^{-1} .

Current density-voltage (J - V) curves were obtained by a source-measurement unit under a simulation with a Xenon lamp (AM 1.5, 55.6 mW cm^{-2} , Newport, Oriel Instruments, USA). The intensity of the incident light was calibrated by a Si-1787 photodiode (Hamamatsu Photonics K K, Hamamatsu, Japan), and the tested area of the solar cells is 0.1 cm^2 . For stability test, the devices were stored under ambient conditions and were tested at selected times without sealing.

For intensity modulated photocurrent/photovoltage spectroscopy measurements, a white light emitting diode (LED) array driven by a Yokogawa 7651 low-noise DC power supply

(Yokogawa, Sugar Land, TX, USA) was used to provide the constant background illumination. A red light ($\lambda = 625$ nm) LED ring was used to provide the sinusoidal optical perturbation signal, whose intensity was modulated by the output of a Stanford SR780 dynamic signal analyzer (Stanford Research Systems, Inc. Sunnyvale, CA, USA). The transfer function module of SR780 was used to detect the IMPS/VIS signals. The intensity of the modulation light was less than 10% of the white light intensity, and the frequency range was set from 100 KHz to 0.1 Hz for both IMPS and IMVS measurements.

3. Results and discussion

3.1 Microstructure and phase structure of TiO₂/PbS/MAPbI₃ films with different SILAR cycles of PbS QDs

Transmission electron microscopy (TEM) images of bare TiO₂, TiO₂/MAPbI₃, and TiO₂/PbS/MAPbI₃ films with 3 and 5 SILAR cycles of PbS QDs are shown in Fig. 2a-d. The micrograph of bare TiO₂ nanoparticles shows a cubic morphology with an average diameter of ~ 20 nm (Fig. 2a). The image of the TiO₂/MAPbI₃ sample shown in Fig. 2b reveals the formation of a continuous MAPbI₃ layer on the surface of TiO₂, which is different from the MAPbI₃ quantum dot structure prepared from the GBL (gamma-Butyrolactone) solution reported previously [21]. The PbS QDs on the TiO₂ surface prepared by 3 SILAR cycles have a spherical morphology with an average diameter of ~ 5 nm, which can be seen in the TEM image shown in Fig. 2c. This image also reveals that the TiO₂ surface is fully covered with the continuous MAPbI₃ film. When the SILAR cycles are increased from 3 to 5, the PbS QD size is increased to ~ 10 nm. The aggregation of the PbS QDs and increased PbS QD coverage on TiO₂ can be seen in Fig. 2d.

Fig. 3a shows the XRD spectra of the TiO₂/PbS/MAPbI₃ films with different SILAR coating cycles (0 - 5) of PbS QDs. The major XRD peaks observed at diffraction angles of

14.04°, 28.40°, and 31.78° are indexed to the (110), (220) and (310) planes of the MAPbI₃ crystal, respectively, suggesting an orthorhombic crystal structure of the halide perovskite [22-24].

Fig. 3b-g show the morphology of the MAPbI₃ films on PbS QD-covered TiO₂ photoanodes with different SILAR cycles. The inset in Fig. 3e shows the EDS element mapping images of the boxed area, which confirms the incorporation of PbS QDs. As shown in Fig. 3b, without PbS QDs the MAPbI₃ film shows an amorphous structure, and small MAPbI₃ particles can be seen in the image. After PbS coating, the MAPbI₃ films show increased MAPbI₃ particle size and more distinct particle boundary (Fig. 3c-g), indicating an increased crystallization in the perovskite films. This improved crystallization could be associated with increased interfacial contacts for MAPbI₃ precursor solution after PbS coating, because the particle size of PbS is much less than that of TiO₂, which present more crystallization sites for the precursor and increase the growth of perovskite crystal. It has been reported that improved perovskite crystallization can benefit light absorption and stability of the material, and thus can promote the overall solar cell performance [25-27].

3.2 UV-Vis-NIR absorption spectra of TiO₂/PbS/MAPbI₃ films with different SILAR cycles of PbS QDs

Fig. 4 shows UV-Vis-NIR spectra of TiO₂/PbS/MAPbI₃ films with different SILAR cycles (0 - 5) of PbS QDs, and the inset shows the absorption intensity dependence on the SILAR coating cycles at wavelengths of 400 and 1000 nm. It can be seen that the TiO₂/PbS/MAPbI₃ films absorb UV-visible light in the wavelength range of 330 to 800 nm, which is mainly associated with the absorption of MAPbI₃ [22]. The absorption onset of MAPbI₃ at ~ 796 nm is observed in Fig. 4, which corresponds to the optical band gap (E_g) of 1.56 eV of MAPbI₃. The absorption onset is determined by finding the intersection point of two slopes as

indicated in Fig. 4, which followed a procedure used in previous studies [24, 28, 29]. After incorporating PbS QDs, the absorption intensity exhibits enhancement in the wavelength range of 330 to 1400 nm, and shows the best improvement for the film prepared with 2 SILAR cycles of PbS QDs. However, further increasing the SILAR cycles beyond 2 results in a decrease in the absorption intensity. The improved absorption intensity for the devices prepared with 1 and 2 SILAR coating cycles could be attributed to the enhanced NIR light absorption due to the incorporation of PbS QDs, as well as the improved crystallization in the MAPbI₃ film that was discussed previously [25,30]. However, when the SILAR coating cycles are further increased, the PbS QD sizes become larger and they also form aggregates on the TiO₂ surface, which, as previous research has shown, can decrease the PbS nanoparticle activity and reduce light absorption [31].

3.3 Photovoltaic properties of perovskite solar cells with different SILAR cycles of PbS QDs

Current density-voltage (J - V) characteristics of the FTO/TiO₂/PbS/MAPbI₃/Pt hybrid solar cells are acquired under simulated solar irradiation, and the results are shown in Fig. 5. The dependence of the short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (η) on SILAR coating cycles are shown in Table 1. It can be seen that the device prepared with 2 SILAR cycles exhibits the best performance, with $J_{sc} = 6.3 \text{ mA cm}^{-2}$, $V_{oc} = 0.88 \text{ V}$, $FF = 0.49$, and $\eta = 4.92\%$. The fill factors of the cells are lower than 0.5, which limits the overall power conversion efficiency. This low FF could be improved by increasing the MAPbI₃ coverage on the photoanode surface. The best efficiency obtained here is 4.92%, which is low compared to those obtained in other studies using similar MAPbI₃ material [27]. However, in this work the solar cell fabrication process is carried out under ambient conditions with a purpose to test the air-processable approach, and improved efficiency of the TiO₂/PbS/MAPbI₃/P3HT solar cells can be expected if the cell

assembly is conducted in a glove box to avoid water and O₂ contaminations as other studies have shown [27].

The V_{oc} of the devices increases from 0.76 to 0.88 V when the PbS coating cycles are increased from 0 to 2, and then starts decreasing when the SILAR cycles are further increased. This change of V_{oc} could be associated with the change of the TiO₂ conduction band (CB) level with different SILAR coating cycles. To better understand this change of V_{oc} as a function of the SILAR coating cycle, cyclic voltammetry (CV) measurement has been performed to estimate the TiO₂ CB levels in the TiO₂/PbS/MAPbI₃ films. Fig. 6 shows the CV measurement results, and the curves exhibit clear reduction peaks. The oxidation peak of the TiO₂ valence band (~ 2.4 V vs. NHE) is not observed because it is not in the range of the test [32]. The CB levels can be calculated using the following equation: $CB\ (eV) = - (E_{onset}^{redox} + 4.64)\ (eV)$, where 4.64 eV is the difference between the vacuum level of normal hydrogen electrode and the potential of the Ag/AgCl electrode (sat. KCl) [33, 34]. E_{onset}^{redox} is the onset reduction potential that is relative to the Ag/AgCl reference electrode [35, 36]. E_{onset}^{redox} and TiO₂ CB levels in the TiO₂/PbS/MAPbI₃ films with different SILAR coating cycles are summarized in Table 2. It can be seen that the onset reduction potentials are negatively shifted when the SILAR coating cycles are increased from 0 to 2, which causes the TiO₂ CB level to shift upwards from -4.41 to -4.13 eV. Further increasing the SILAR coating cycles leads to a positive shift of the onset reduction potential, which causes the TiO₂ CB level to shift downwards as shown in Table 2. The results obtained in the CV analysis indicate that the TiO₂ CB level is highly dependent on the SILAR coating cycle, which is important for the design of PbS/MAPbI₃-based hybrid solar cells. Conduction band edge position is a key factor that determines V_{oc} , and an upshift (downshift) of the TiO₂ CB level can lead to an increase (decrease) in V_{oc} [37]. Therefore, the change of V_{oc} shown in Table 1 could be associated with the corresponding change of the TiO₂ CB energy level in the cells.

Fig. 7 shows the normalized power conversion efficiency as a function of aging time for selected $\text{TiO}_2/\text{PbS}/\text{MAPbI}_3/\text{P3HT}/\text{Pt}$ solar cells, which are measured after storing the cells under ambient conditions without sealing. It can be seen that the normalized efficiency of the cell without PbS QDs shows a 70% decrease after 97 h, while that of the cell with 2 SILAR cycles of PbS QDs only exhibits an 18% decrease under the same storage and measurement conditions. It has been reported that the photocatalytic effect of TiO_2 can extract electron from Γ in MAPbI_3 and cause decomposition of MAPbI_3 , which damages the stability of the perovskite film [13]. In our experiment, it is also observed that the MAPbI_3 film coated on pure TiO_2 surface turns to yellow gradually, while the one coated on the surface of bare FTO glass substrate keeps the original black color under the same storage conditions, which manifests the TiO_2 decomposition effect. As **Fig. 7** suggests, inserting a PbS QD layer between TiO_2 and MAPbI_3 could reduce the TiO_2 photocatalytic effect and associated decomposition damage to the MAPbI_3 film, and thus could improve the device stability.

3.4 Intensity modulated photocurrent/photovoltage spectroscopy of perovskite solar cells with different SILAR cycles of PbS QDs

IMPS/VS measurements are performed to study the charge transfer and recombination processes in the perovskite solar cells, and **Fig. 8a and b** show the obtained IMPS and IMVS curves, respectively. The electron transport time constant τ_c can be calculated using the equation $\tau_c = 1/2\pi f_c$, where f_c is the characteristic frequency minimum of an IMPS curve (**Fig. 8a**) [18]. The electron diffusion coefficient D_n can be estimated from τ_c using $D_n = \omega^2/(2.35\tau_c)$, where ω is the thickness of the photoanode film and $\omega = 0.5 \mu\text{m}$ for the cells studied here [38]. **Fig. 8c and d** show the electron transport time constants and electron diffusion coefficients of the perovskite solar cells with different SILAR coating cycles, respectively. It can be seen that compared to the cell without PbS coating, after incorporating

PbS QDs the cells exhibit improved τ_c and D_n values, suggesting enhanced electron diffusion in the modified perovskite solar cells [39]. Fig. 8e shows the electron recombination time constant τ_r as a function of the SILAR coating cycle, which is calculated using $\tau_r = 1/2\pi f_r$, where f_r is the characteristic frequency minimum of an IMVS curve (Fig. 8b) [18]. The increased τ_r from 0 to 2 SILAR cycles suggests an improved electron recombination process in the perovskite solar cells, and this could be attributed to the blocking effect of the PbS layer as the coverage of PbS QDs on TiO_2 surface increases, which could reduce electron recombination between TiO_2 and MAPbI_3 . However, when the SILAR cycles are further increased, the PbS QDs start to form aggregates, which could increase the number of trap sites in the device structure and lead to higher possibilities for electron recombination and hence decreased recombination time constant [40]. In addition, it can be seen from Fig. 2c and d that the PbS QD size increases from ~ 5 nm to ~ 10 nm as the SILAR cycles are increased from 3 to 5. Due to the relationship between particle size and quantized energy levels in QDs, increasing PbS particle size leads to decreased PbS band gap and downshift of the PbS conduction band level [41]. For example, the PbS QD with a particle size of 5 nm has a CB level of -4.0 eV, while the one with a particle size of 10 nm has a CB level of -4.4 eV that is lower than that of TiO_2 (-4.2 eV) [42,43]. This downshift of PbS CB level causes mismatched CB levels between PbS and TiO_2 , which could hamper electron transfer from PbS to TiO_2 and result in increased electron recombination in the cell.

The electron diffusion length L represents the average distance an electron travels before it recombines with either the oxidized sensitizer or the hole transport material in a solar cell, and a longer L allows the usage of a thicker photoanode film and hence more sensitizer loading, which can promote the power conversion efficiency [17,44]. L can be calculated from the diffusion coefficient and recombination time constant using $L = (D_n \cdot \tau_r)^{1/2}$, and Fig. 8f shows the diffusion length as a function of the SILAR coating cycle obtained in this work

[38]. In dye-sensitized solar cell, it is well known that the electron diffusion length needs to be larger than the TiO_2 film thickness in order to have an efficient collection of photo-generated electrons [45]. From Fig. 8f it can be seen that the perovskite solar cell without PbS coating has a L value of $0.29\ \mu\text{m}$, which is smaller than the TiO_2 film thickness ($0.5\ \mu\text{m}$). All the other cells that have PbS coating exhibit L values larger than the TiO_2 film thickness, with the highest L value of $0.86\ \mu\text{m}$ obtained for the device prepared with 2 SILAR cycles of PbS QDs. This suggests that the PbS coating could improve the charge diffusion length in the perovskite solar cells, which could be attributed to the improved electron transport and reduced electron recombination processes as suggested by Fig. 8c and e [46]. Recent studies have shown that the charge diffusion length can be longer than $1\ \mu\text{m}$ for planar-type perovskite solar cells based on $\text{MAPbI}_{3-x}\text{Cl}_x$; however, to the best of our knowledge, for perovskite solar cells based on MAPbI_3 it is typically only $\sim 0.1\ \mu\text{m}$ except one recent report [14,16,17]. The best L value of $0.86\ \mu\text{m}$ obtained in this work is substantially larger than the aforementioned value, suggesting that incorporating PbS QDs could be an efficient way to enhance the charge diffusion length in MAPbI_3 -based perovskite solar cells.

4. Conclusions

In summary, hybrid perovskite solar cells prepared with PbS QDs are studied in this work. The incorporation of PbS QDs between TiO_2 and MAPbI_3 could improve the crystallization of MAPbI_3 film and enhance light absorption. The effects of the SILAR coating cycle on solar cell performance are inspected, and the device prepared with 2 SILAR cycles exhibits the best performance. It is also found that the long-term stability of the PbS QD-modified perovskite solar cells, as measured over 97 hours under ambient conditions without sealing, is much better than that of the cell without PbS QDs, suggesting a protective effect of the PbS

coating that could decrease the TiO_2 decomposition damage to the MAPbI_3 film. Charge transfer dynamics in the perovskite solar cells is studied using the IMPS/VS measurement technique, and substantially enhanced charge diffusion lengths are obtained for the cells modified with PbS QDs. This improvement in diffusion length could be associated with improved electron transport and reduced electron recombination after incorporating PbS QDs. Further improvement in solar cell performance could be expected through optimization of the device fabrication process, such as assembling the cells in a glove box to avoid water and O_2 contaminations as well as employing counter electrodes with better energy level matching and electro-catalytic activities [47].

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Figure captions:

Fig. 1. (a) Schematic of the hybrid perovskite solar cell based on $\text{TiO}_2/\text{PbS}/\text{MAPbI}_3/\text{P3HT}/\text{Pt}$;

(b) The energy level alignment in the hybrid perovskite solar cell.

Fig. 2. TEM images of (a) bare TiO_2 , (b) $\text{TiO}_2/\text{MAPbI}_3$, (c) TiO_2/PbS (3 cycles)/ MAPbI_3 , and (d) TiO_2/PbS (5 cycles)/ MAPbI_3 films.

Fig. 3. (a) X-ray diffraction spectra of $\text{TiO}_2/\text{PbS}/\text{MAPbI}_3$ films with different SILAR cycles of PbS (0 - 5 cycles). SEM images of (b) $\text{TiO}_2/\text{MAPbI}_3$, (c) TiO_2/PbS (1)/ MAPbI_3 , (d) TiO_2/PbS (2)/ MAPbI_3 , (e) TiO_2/PbS (3)/ MAPbI_3 , (f) TiO_2/PbS (4)/ MAPbI_3 , and (g) TiO_2/PbS (5)/ MAPbI_3 films. The inset in (e) shows the EDS element mapping images of the boxed area.

Fig. 4. UV-Vis-NIR absorption spectra of TiO_2/PbS (0 - 5cycles)/ MAPbI_3 films. The inset shows the absorption intensity dependence on the PbS coating cycles at wavelengths of 400 and 1000 nm.

Fig. 5. J - V curves of perovskite solar cells with different SILAR cycles of PbS (marked as MAPbI_3 and PbS (1-5)/ MAPbI_3)

Fig. 6. Cyclic voltammograms of $\text{TiO}_2/\text{PbS}/\text{MAPbI}_3$ electrodes with different SILAR cycles in $\text{LiClO}_4/2$ -propanol. The effective area of the TiO_2 nanoporous electrode is 0.5 cm^2 . The arrow indicates the positive scan.

Fig. 7. Normalized power conversion efficiency as a function of aging time for the perovskite solar cells based on MAPbI_3 and PbS (2 cycles)/ MAPbI_3 .

Fig. 8. (a) IMPS and (b) IMVS spectra of perovskite solar cells based on $\text{PbS}/\text{MAPbI}_3$ films with different SILAR cycles. The dependence of (c) electron transport time constant, (d) electron diffusion coefficient, (e) electron recombination time constant, and (f) electron diffusion length on the SILAR coating cycles.

Table Captions

Table 1. J_{sc} , V_{oc} , FF, and η of perovskite solar cells with different SILAR cycles of PbS.

Table 2. Conduction band values of PbS/MAPbI₃ co-sensitized TiO₂ photoanodes with different SILAR cycles determined by CV measurements.

Table 1

	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	η (%)
MAPbI ₃	4.06	0.76	0.345	1.91
PbS (1)/MAPbI ₃	4.54	0.74	0.358	2.16
PbS (2)/MAPbI ₃	6.30	0.88	0.493	4.92
PbS (3)/MAPbI ₃	3.97	0.84	0.414	2.49
PbS (4)/MAPbI ₃	1.99	0.82	0.460	1.35
PbS (5)/MAPbI ₃	1.36	0.62	0.305	0.46

Table 2

	TiO ₂ / MAPbI ₃	TiO ₂ /PbS(1) /MAPbI ₃	TiO ₂ /PbS(2) /MAPbI ₃	TiO ₂ /PbS(3) /MAPbI ₃	TiO ₂ /PbS(4) /MAPbI ₃	TiO ₂ /PbS(5) /MAPbI ₃
<i>E</i> _{onset} ^{redox} (V)	-0.23	-0.29	-0.51	-0.35	-0.28	-0.24
CB(eV)	-4.41	-4.35	-4.13	-4.29	-4.36	-4.40

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8