

Downshifting Electron Transport Layer for efficiency and UV-stability enhancement of planar perovskite solar cells

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Introduction

The recent decade has witnessed the rapid increase of the power conversion efficiency (PCE) of metal halide perovskite solar cells (PSCs) from 3.8% to certified 25.5% [1]. Despite their success in achieving intriguing photovoltaic (PV) performance, the operational stability of PSCs against external stimuli remains critical hurdles for their further large-scale applications. For example, the high-energy photons from the UV portion of solar spectrum can induce the dissociation of perovskite materials into metal halide and halogen via a superoxide-mediated pathway. In addition, titanium dioxide (TiO₂), which is widely used as electron transport materials (ETMs) in high-efficiency PSCs, would trigger interfacial photocatalytic reaction of perovskite films under continuous UV light exposure [2]. While considerable research efforts have been devoted to prolonging the device lifespan of PSCs in humid environment, the inferior stability of PSCs when coupling with the penetrated UV light remains an unresolved problem.

Results

In this study, we developed a luminescent ETM composed of Europium-doped TiO₂ (Eu-TiO₂) via a low-temperature chemical-bath deposition (CBD) approach, which not only serve as an efficient charge transport layer but also effectively downshift damaging UV light to extra visible luminescence [3]. As illustrated in Figure 1a, high-energy UV photons were firstly absorbed by the TiO₂ host matrix, and then relaxed to the Eu³⁺ activator, subsequently emitting efficient visible luminescence via the intra-4f transitions between the Russell-Saunders multiplets ⁵D₀ to ⁷F_j (j = 0, 1, 2, 3, 4). To verify the down-shifting effect of Eu-TiO₂, the steady-state photoluminescence (PL) spectra of TiO₂ and Eu-TiO₂ films were measured upon 360 nm UV light excitation (Figure 1b). The Eu-TiO₂ film showed several featured PL emission peaks with a dominant red emission peak at 615 nm associated with the electric-dipole ⁵D₀-⁷F₂ transition, while that of the TiO₂ film did not show any peaks in the visible light region (Figure 1c). The controllable doping of Eu³⁺ also leads to a more optimized energy band alignment and therefore facilitates the electron extraction of Eu-TiO₂-based PSCs (Figure 1d). As a result, the use of Eu-TiO₂ as ETM in planar PSCs leads to 5% increase in photocurrent and yields a high PCE of 21.40%, as shown in Figure 2a-b and summarized in Table 1.

Notably, the device based on Eu-TiO₂ films displayed much higher *EQE* values with an enhanced integrated photocurrent by ~0.4 mA cm⁻² in the UV region (< 400 nm), revealing the photocurrent contribution from the down-shifting luminescence (Figure 2c). To further confirm the impact of the down-shifting effect on photocurrent, we deliberately exposed PSCs based on both TiO₂ (8 devices) and Eu-TiO₂ films (8 devices) under pristine UV light illumination with a high intensity of 10 mW cm⁻², and measured their *J-V* curves. As shown in Figure 2d, devices based on Eu-TiO₂ films delivered an average *J_{sc}* of 1.67 mA cm⁻², which is over two times higher than that of TiO₂ films (0.52 mA cm⁻²), highlighting the photocurrent contribution from the luminescence converted from UV light by the Eu-TiO₂ layer.

More encouragingly, PSCs based on Eu-TiO₂ exhibit remarkably improved UV stability, retaining about 75% of the original PCE after aging for 500 hours under continuous UV light illumination (5 mW cm⁻²) in ambient conditions with a relative humidity (RH) level of 60±10%, while the control device with pristine TiO₂ lost the majority of the initial PCE after aging for 150 hours (Figure 2e) in the same aging conditions. With the gradual dissociation of bulk perovskite films as well as the interfacial degradation accelerated by the photocatalytic TiO₂, the control devices experienced rapid photocurrent decay under UV illumination (Figure 2f). In the case of downshifting Eu-TiO₂ films, the corrosive UV photons that drives the decomposition of perovskite films can be effectively converted

to visible luminescence and simultaneously contribute to the enhanced light harvesting, leading to much improved UV stability of PSCs based on bifunctional Eu-TiO₂ ETMs.

Conclusions

In summary, we report a luminescent Eu-TiO₂ ETM for efficient and UV-stable n-i-p planar PSCs. Benefiting from the enhanced light harvesting by down-shifting effect and a more optimal energy band alignment, PSCs based on Eu-TiO₂ films deliver a boosted PCE of 21.40%. In addition, these Eu-TiO₂ devices exhibit significantly improved UV and operational stability in ambient condition (RH 60±10%). Our findings offer an effective way to simultaneously improve the UV-stability and efficiency of PSCs, and this facile strategy is also applicable to other perovskite-based optoelectronic devices beyond photovoltaics.

Table I. Summary of the best photovoltaic performance of the fabricated PSCs based on TiO₂ and Eu-TiO₂ films with different Eu doping ratios.

ETM	PCE (%) [*]	J _{sc} (mA cm ⁻²) [*]	V _{oc} (V) [*]	FF [*]
Control	18.58 ± 0.74 (19.22)	22.20 ± 0.95 (22.28)	1.09 ± 0.03 (1.12)	0.76 ± 0.02 (0.77)
2.5% Eu	19.24 ± 0.96 (20.20)	22.79 ± 0.77 (23.56)	1.10 ± 0.02 (1.10)	0.76 ± 0.02 (0.78)
5% Eu	20.13 ± 1.27 (21.40)	23.32 ± 0.68 (23.85)	1.12 ± 0.03 (1.13)	0.76 ± 0.03 (0.79)
8% Eu	17.97 ± 1.08 (19.05)	22.07 ± 0.99 (21.95)	1.10 ± 0.02 (1.10)	0.74 ± 0.05 (0.79)

^{*}Average values with standard deviation are obtained from 28 devices, and the values in brackets are the photovoltaic parameters of the champion devices.

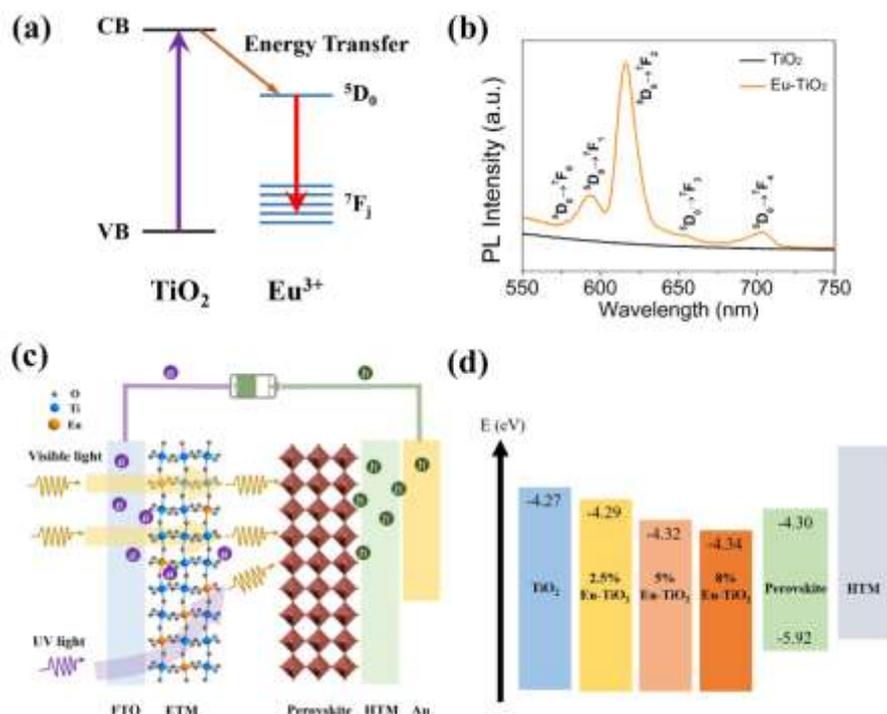


Figure 1. (a) Illustrated mechanism of down-shifting transition of Eu-TiO₂ films from UV photons to visible luminescence, (b) the steady-state PL spectra of TiO₂ and Eu-TiO₂ films on glass, (c) Schematic illustrations of the device configuration of n-i-p planar PSCs employing Eu-TiO₂, (d) energy band alignment diagram of different layers of PSCs.

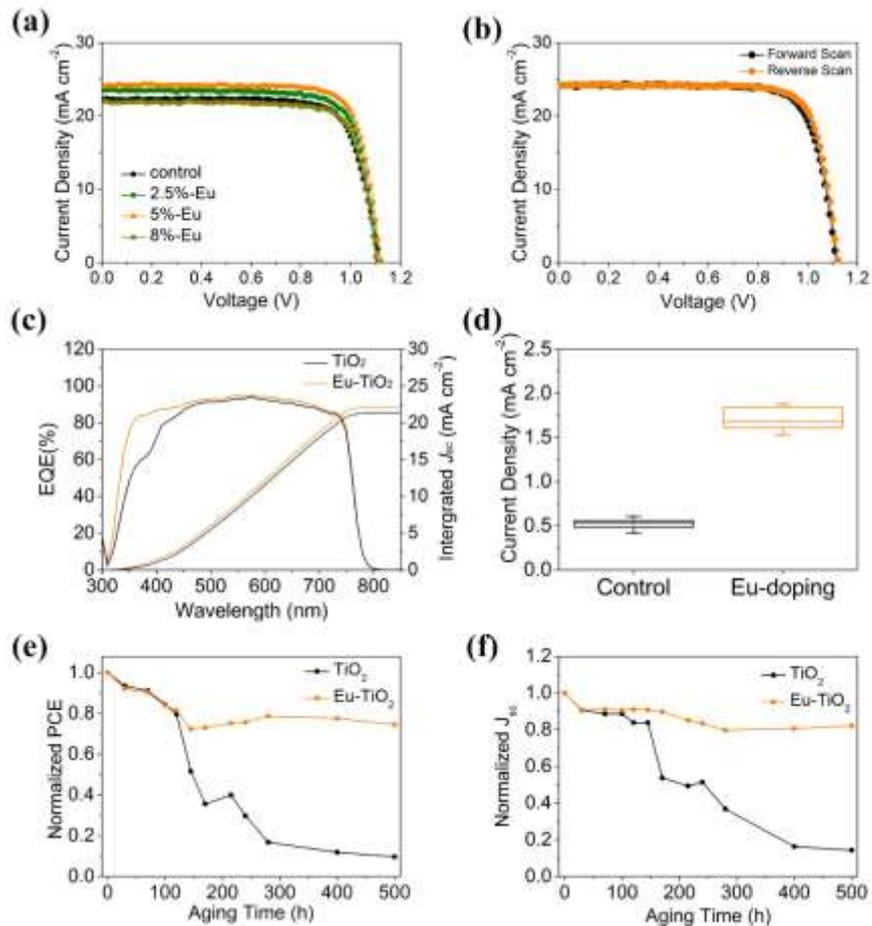


Figure 2. (a) The J - V curves of PSCs based on TiO_2 , 2.5% Eu-TiO_2 , 5% Eu-TiO_2 , and 8% Eu-TiO_2 films, (b) the J - V curves of the champion device based on 5% Eu-TiO_2 film under forward and reverse scans, (c) IPCE measurement and the integrated J_{sc} of PSCs based on TiO_2 and 5% Eu-TiO_2 films, (d) the average photocurrent of PSCs based on TiO_2 and 5% Eu-TiO_2 films under intensive UV illumination (10 mW cm^{-2}), (e) the stability testing of the encapsulated PSCs based on TiO_2 and Eu-TiO_2 films exposing under continuous UV illumination in ambient conditions ($\text{RH } 60 \pm 10\%$), (f) the evolved J_{sc} of PSCs based on TiO_2 and Eu-TiO_2 films under continuous UV light illumination.

References

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